Chem. Rev. **2002,** *102,* 1551–1593

Selective Alkane Transformations via Radicals and Radical Cations: Insights into the Activation Step from Experiment and Theory

Andrey A. Fokin*,† and Peter R. Schreiner*,‡

Department of Organic Chemistry, Kiev Polytechnic Institute, 37 Pobedy Avenue, 03056 Kiev, Ukraine, Department of Chemistry,
University of Georgia, Athens, Georgia 30602-2556

Received September 6, 2001

Contents

1. Introduction

As the main constituent of natural gas, alkanes are arguably Nature's most plentiful organic base chemicals that are easily accessible. Chemists have long coveted the use of alkanes as feedstock for clean-burning fuels, plastics, solvents, new materials, and even pharmaceuticals. Hence, the selective functionalization of aliphatic hydrocarbons is a major challenge and is considered a "holy grail" in chemistry.[1,2] In view of an increasing energy consumption (*California's calling*) and the ever growing demand for bulk chemicals, solving this problem is not only essential for the petrochemical industry but also needs to be addressed in view of the fact that about 90% of all alkanes are simply burned, although they could serve as abundant feedstocks for the chemical industry rather than being a major contributor to global warming.

Alkanes are usually the first organic compounds students hear or read about, and they are usually described as unreactive (affinity to little = *parum affinis*, paraffins) and, apart from being solvents and fossil fuel components, as not particularly useful. The students are then very often told that this is because it is difficult to activate alkanes, i.e., the C−H bonds are very strong and reluctant to react. This of course paints an inadequate picture because *activation* is not so much of a problem as alkanes react readily with a large variety of compounds: radicals, carbenes, organometallic species, the proton, carbocations, superacids, peroxides, and many others.[3−12] However, selective *functionalization*, i.e., the targeted substitution of a C−H to a C−X bond, proves rather difficult[13−21] because the products are almost inevitably more reactive than the starting materials; the regioselectivities usually are rather low and display little discrimination of primary, secondary, and tertiary C−H bonds. To illustrate this point further, consider traditional electrophilic alkane chemistry:

---

† Kiev Polytechnic Institute. E-mail: aaf@xtf.ntu-kpi.kiev.ua.
‡ University of Georgia. E-mail: prs@chem.uga.edu.

10.1021/cr000453m CCC: $39.75

The above picture does not, as some readers may have suspected, show the authors' tired faces after writing the present review. Rather, this shot was taken during a recent hiking trip requiring similarly demanding tasks.

Andrey A. Fokin (left) is Professor of organic chemistry at the National Technical University of Ukraine "Kiev Polythechnic Institute". He obtained his Candidate (1985) and Doctor (1995) of Chemical Sciences degrees from this institution. He was a DAAD (1996) and Alexander von Humboldt (1997–1998) research fellow in the group of Professor P. v. R. Schleyer at the University of Erlangen-Nürnberg (Germany). He is the author of more than 100 publications on the chemistry of cage compounds, pesticide chemistry, alkane activation mechanisms, computational chemistry of radicals and radical ions, and the gererations as well transformations of hydrocarbon radical cations.

Peter R. Schreiner (right) is Professor of organic chemistry at the University of Georgia, Athens. He studied chemistry in his native city at the University of Erlangen-Nürnberg, Germany, where he received his Dipl. Chem. (1992) and Dr. rer. nat. (1994) in Organic Chemistry with P. v. R. Schleyer. Simultaneously, he received a Ph.D. degree (1995) with H. F. Schaefer III in Computational Chemistry from the University of Georgia. His Habilitation, dealing with the experimental and computational aspects of alkane activation as well as of endiyne and enyne–allene cyclization reactions, was completed at the University of Göttingen (1999) in the group of A. de Meijere. His research interests are diverse and include, apart from the aforementioned topics, hydrogen-bonded catalysis, phase-transfer catalysis, and chirality. Among other awards, he received the ADUC-Prize for Habilitanden 1999, was a Liebig-Fellow (1997–1999), and held a Habilitandenstipendium of the DFG (1999). He serves as an Assistant Editor for the *Journal of Computational Chemistry* and as a section editor and the project coordinator for the *Encyclopedia of Computational Chemistry*.

when reacted with superelectrophilic halogens (e.g., SbF_5/Cl_2), *n*-butane and isobutane give approximately the same mixtures of monosubstituted products,[13] that is, the overall reaction functionalization *is* selective (predictably giving one major product) but the activation is *not* (different cations are generated and equilibrate rapidly). Very often, this clear-cut distinction is not made and the terms "activation" and "functionalization" are used interchangeably.

Selectivity problems in the activation step can be overcome by well-chosen reaction conditions such as heterogeneous metal surfaces or inorganic materials such as zeolites,[22−29] homogeneous transformations with low-valent, electron-deficient transition-metal complexes.[2,30] As the steric hindrance is often increased in the products, these do not bind to the metal as effectively as the parent alkane, leading to considerably high chemo- and regioselectivities.[1,16] However, only a few heterogeneous alkane transformations are used industrially[31] due to inherent practical limitations (low conversions, high energy consumption, and others). Some more recent approaches to alkane activation include σ-bond metathesis with noble metals[32−35] and electron-deficient borane derivatives.[36,37] Despite the success and synthetic beauty of these organometallic transformations, they are not yet of high practical value because the preparative procedures are quite demanding and do not immediately lend themselves to large-scale production.

Nature is far more advanced when it comes to transforming alkanes to some more useful derivatives. She has developed highly selective and efficient catalytic systems which chemists currently are elucidating and mimicking. Such systems include, among others, cytochrome P450,[38] methane monooxygenases (MMO),[39,40] and some other enzymes.[41,42] We will include these systems in our discussion where appropriate to demonstrate the similarities between these and purely chemical (laboratory) systems. While this review focuses on mechanistic aspects of alkane radical activations, the implications are far-reaching, including autoxidations,[43−49] combustion,[50] and atmospheric chemistry.[51−58]

Alkane activation mechanisms are not as simple as they may appear.[39,59] For instance, although the C−H BDEs of many alkanes are very well-known,[60,61] there is often only a modest correlation with the rates for H-abstraction.[62,63] Apart from other factors this is frequently due to the formation of initial complexes[64,65] between the hydrocarbon and the activating species, as expressed in the often found non-Arrhenius kinetics and negative temperature coefficients for the C−H activation step. This behavior is also reflected in the H/D kinetic isotope effects (KIEs)[66−76] which vary largely for the same type of substrate and sometimes are much higher than the semiclassical limit,[66] especially in enzymatic systems.[77,78]

Theory has become an indispensable tool to examine and elucidate alkane activation mechanisms, in particular, when combined directly with high-quality experimental measurements. For instance, KIEs directly relate computed[79−82] transition structures with measured rate differences for C−H vs C−D bond activations. Theory also provides detailed information on the interacting orbitals, the polarization of the reactants, as well as individual bonds or atoms and allows predictions to be made. Computations help refine classical empirical and semiempirical approaches[83−87] by providing better parameters, e.g., BDEs,[88−91] strain energies,[92] electronegativities,[93,94] polarizations, etc.[95] Nevertheless, computational approaches are by no means fail-safe; after all, the reactions in the forthcoming review involve both closed- and open-shell molecules where it is obvious that a proper treatment of electron correlation is necessary.[96] Early computations on barriers and rate constants for H-abstraction reactions[97] gave unsatisfactory results. Perturbative treatments of electron correlation such as Møller−Plesset levels of theory (MP,[98] UMHF,[99] and MRMP[100]) generally suffer from spin contamination,[101,102] making them equally error prone for reactions involving open-shell species. Higher-level correlation treatments certainly do much better but still are not feasible for large systems. A promising alternative may be offered by density functional theory (DFT) approaches[68,103−107] which in some regard turn out to be the "jack of all trades" when it comes to radicals.[96,108] Systematic studies on the H-abstraction reactions from different types of molecules with radicals show that "*DFT methods produce barriers that are in better agreement with experimental values than those calculated by HF and MP2 methods*"[109] and "*...pre-exponential factors and even the curvature of the Arrhenius plots are accurately predicted by transition-state theory using DFT parameters*".[110] Generally, DFT offers a very good compromise between accuracy and computational effort. These methods can be applied successfully to the modeling of alkane activations ranging from transition metals[111] to enzymatic systems.[112,113] DFT can be also used in verifying new mechanistic concepts in alkane activation chemistry such as the most recent two-state reactivity model.[114−118] Meanwhile, new functionals for open-shell species[119] as well as new basis sets[120] were developed to improve their accuracy and apparent resistance to spin contamination even further. Finally, molecular dynamics (MD) calculations, which provide data going far beyond static electronic structure theory approaches, also have improved considerably.[64,121] MD calculations are now able to reproduce the experimental rate constants quite accurately for selected H-transfer reactions of limited dimensionality of their potential energy hypersurfaces.[122−124]

Rate constants for H-atom abstractions from hydrocarbons depend on the solvent only slightly,[125,126] in contrast to H-bonding substrates such as phenols[127] where rate constants are highly solvent-dependent but independent of the abstracting radical so that the rates "*can be accurately predicted in any of several hundreds of solvents*".[84] An explanation of the negligible effect of solvent polarity on the rates of H-abstractions from hydrocarbons even with electrophilic[128] radicals (which certainly occur via polar transition states) can be associated with "*the assumption of the solvent not having sufficient time to adapt to the polarization of the transition state*"[126] because C−H breakage is driven by a "*...predominant charge-transfer component*"[126] with substantial contribution of radical cationic states of the hydrocarbon ($^{\bullet}RH^{+}\cdots X^{-}$ and $^{+}RH^{\bullet}\cdots X^{-}$).[129] Using bonding/antibonding Morse curves for hydrogen-abstraction reactions[130] it was shown that polar contributions[131] do exist as to "*the strength of the bond being broken and made is not a major factor*" in predicting of activation barriers for H-abstraction,[132,133] that "*...the rate is primarily influenced by polar factors...*",[86] and "*...the transition-state energy for hydrogen atom abstraction is lowered ...by increasing the electron deficiency...*".[134] Curve crossing models[135] based on quantitative ab initio data give reaction profiles, and polar effects for the reaction with electrophilic radicals can be estimated from the relative weights of the $D^{+}A^{-}$ configurations.[63,136−138]

The present review covers radical as well as single-electron-transfer chemistry because the authors feel that these are at different ends of the same mechanistic spectrum. Mechanistically, the C−H abstraction reactions with radicals have some common features with the interactions of electrophiles with alkanes. It was noted in the C−H activations with carbocations that "*the hydrogen being transferred has a large amount of radical character*",[138] at least for such symmetrical systems such as $CH_4 + CH_3^{+} \rightarrow CH_3^{+} + CH_4$, and that the reactivity of R^{+} and $R^{\bullet}$ are "*closely related*".[139] In a number of so-called "hydride transfer reactions" in alkane chemistry[138,140−147] $R{-}H + X^{+} \rightarrow [R\cdots H\cdots X]^{+} \rightarrow R^{+} + H{-}X$, the transferred hydrogen formally does not carry a (partial) negative charge due to the usually higher electronegativities of both carbon and X. As a matter of fact, the hydrogen is neutral or slightly *positively* charged in these types of transition structures and "*the probability of having two electrons on the H being transferred is not reflected separately neither in the intracule nor in the extracule* (density) *distributions*".[148] Hence, the only difference from radical (or other uncharged) abstractors is that in the reactions with electrophiles the transfer of net charge removed from the hydrocarbon moiety is higher than that for electrophilic radicals (vide supra) due to the increased contributions of the $^{+}R{-}H^{\bullet}\cdots X^{\bullet}$ and $^{\bullet}R{-}H^{+}\cdots X^{\bullet}$ resonance states. A more realistic mechanistic scenario may result in the superposition of two situations: synchronous hydride transfer (SHT) and single electron transfer (SET). It was shown that "*...SHT exhibits characteristics of an electron-transfer process without actually being an SET process*",[149] even for nonoxidizing electrophiles. For oxidizing electrophiles the situation may be entirely different and ET may dominate;[150] hydrocarbon radical cation intermediates form. The SHT/SET dichotomy[151−156] (i.e., one-electron vs two-electron transfers) plays a role in a number of organic reactions[157,158] and is especially important for modeling biological systems.[141,159−162]

The structure of this review reflects this mechanistic understanding as it first covers radical chemistry, moving from traditional reagents to electrophilic radical-like species. The structures of σ-radical cations generated from different sources follow next, including the reactions of SET-oxidizers of low electrophilicity. As there are excellent reviews on superacidic alkane activations[13−15,18,163−167] and the use of transition metals for C−H insertions into hydrocarbon bonds,[16,20,21,30,168−171] we will not cover these here. Since there is still limited insight into the mechanisms of alkane activation reactions, we will emphasize the very fruitful combination of experiment and theory in elucidating these.

2. Alkane Activations with Radicals

$$\mathbf{R{-}H + X^{\bullet} \rightarrow R^{\bullet} + H{-}X}$$

2.1. Halogen Radicals

Alkane halogenation reactions with elementary free radicals are some of the oldest chemical reactions, so it is often overlooked that these transformations are neither particularly selective nor broadly applicable. Fluorinations occur explosively and are difficult to control; chlorinations are more moderately exothermic but also lead to product mixtures. Brominations are endothermic in the H-abstraction step

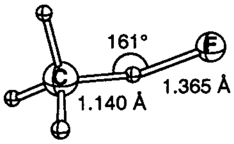


Figure 1. MP2/6-31G(*d*,*p*)-optimized geometry of the TS for the H-abstraction from methane by the F radical.[179]

and hence somewhat easier to control. Higher halogenation products (for instance, the environmental culprit carbon tetrachloride in chlorinations) often are undesirable byproducts and must be appropriately disposed. As these halogenation reactions are thermodynamically driven, sensitive hydrocarbons undergo cracking, isomerization, or oligomerization, making this procedure very often entirely useless for strained alkanes.[172] Iodinations of unstrained paraffins with I_2 are not possible using this route due to their overall endergonicity. Despite decades of research and because of the continued interest in halogen radicals as key atmospheric reactive intermediates, the reactions of halogen radicals are still under intense investigation. There is a plethora of experimental and computational data on their reactions with aliphatics (and, of course, many other compounds) which are reviewed in the following.

2.1.1. Fluorine Radical

Studies of hydrogen-abstraction reactions by fluorine radicals mostly are motivated by research on decomposition of fluorine-containing waste materials, tropospheric photooxidations of hydrohaloalkanes (Freons), chemically pumped HF lasers, as well as the necessity to substitute the traditional chlorine-containing Freons (CCl_2F_2, $CHClF_2$) by hydrofluorocarbons. Perfluorinated alkanes are also increasingly popular as unique solvents for multiphase-catalyzed organometallic transformations.[173]

The simplest reaction $F^\bullet + CH_4 \rightarrow H_3C^\bullet + HF$ was studied in detail both experimentally and computationally. The experimental rate constants are in range from 4×10^{-11} to 10×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K[174,175] (the recommended values are $(6.8 \pm 1.4) \times 10^{-11}$ [176] and $(6.7 \pm 0.4) \times 10^{-11}$ [177] cm^3 $molecule^{-1}$ s^{-1}), and these are characteristic of low activation barriers. Earlier MNDO and SCF Hartree–Fock (HF) computations[178] suggested C_{3v}-symmetric transition structures for hydrogen abstraction with C–H distances of 1.159 Å (MNDO) and 1.311 Å (HF/3-21G); the barriers were strongly overestimated. More recent MP2 and QCISD/6-31G(*d*,*p*) results show[179] that the PES around the TS is fairly flat and that the computed barriers are around 1.0–1.4 kcal mol^{-1} at these levels. The TS for hydrogen abstraction (Figure 1), in contrast to the other halogen radicals (vide infra), is nonlinear (C–H–F = 161°) with C–H and H–F distances of 1.140 and 1.365 Å. Such deviations from linearity were rationalized by hyperconjugative interactions between the fluorine lone pairs and the C–H bonds.[179] Both the MP2 and QCISD computations reproduce the large experimental reaction enthalpy (−32.0 kcal mol^{-1}) well; the rate constants calculated at the QCISD level using variational transition-state theory also agree with the experimental data.

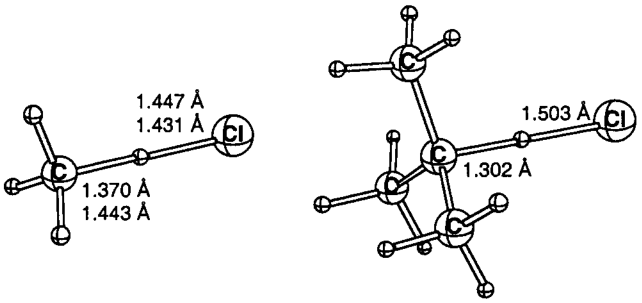


Figure 2. Geometries for the TS of H-abstraction from methane (MP2/6-311G(2*d*,*d*,*p*) (first line)[193] and BH&HLYP/6-311G(*d*,*p*) (second line))[195] and isobutane (MP2/6-31G(*d*,*p*), present work) by Cl radical.

Halomethanes have lower C–H abstraction rates (e.g., 1.7×10^{-11}, 2.6×10^{-11}, 3.1×10^{-11}, and 1.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for CHF_nCl_m,[180] CF_3CH_2F,[181] CH_3Br,[182] and CH_2BrCl,[183] respectively) and similarly low barriers (2.9 kcal mol^{-1} for CHF_3 and 1.1 kcal mol^{-1} for $CHCl_3$).[180] Hence, perfluorination of methane is unfavorable and halts at the stage of fluoroform in oxidative fluorinations.[184] The geometrical parameters of the corresponding TSs also depend on the number of fluorine atoms in CHF_nCl_m: the critical F–H distances increase with fluorine incorporation, i.e., the transition structures become more product-like.[185] The deviations of the PMP2/6-311G(2*d*,2*p*) barriers from the experimental values are relatively small (≤1.0 kcal mol^{-1}), in contrast to PMP2/6-31G(*d*,*p*) which overestimates the barrier by about 2 kcal mol^{-1}.[185]

Fluorination of higher alkanes (ethane, isobutane) is also characterized by very low barriers (around 0.7 kcal mol^{-1}). The computed barriers strongly depend on the level used; MP4/6-31G(*d*)//MP2/6-31G(*d*) single-point energy calculations improve the results.[186] The rate constant for the $F^\bullet + C_2H_6$ reaction was measured relative to $F^\bullet + H_2$.[187]

2.1.2. Chlorine Radical

The free-radical chlorination of alkanes is one of the oldest[188] and most well-studied reactions in organic chemistry and still is industrially useful for methane.[21] The occurrence of these reactions in the atmosphere,[189–191] contributing to ozone depletion, warrants their detailed experimental and high-level computational studies.

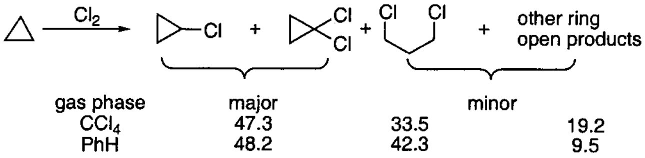
The TS for H-abstraction from methane (Figure 2) with the chlorine radical is, in contrast to fluorine, linear[192] and the C–H bond is longer[193] (from 1.375 Å at MP2/TZ+2P[194] to 1.443 Å at BH&HLYP/6-311G(*d*,*p*)[195]) than in the C–H–F TS moiety. The computed MP4/6-31+G(*d*,*p*)//MP2/6-31+G(*d*,*p*) barrier (3.4 kcal mol^{-1})[192] is in excellent agreement with the experimental[196] value in the range of 360–500 K. To estimate the rate constants correctly,[197] tunneling effects must be taken into account which increase the rate constants for the $CH_4 + Cl^\bullet \rightarrow H_3C^\bullet + HCl$ reaction by a factor of 3.[198] Detailed studies on the observed non-Arrhenius behavior of the $CH_4 + Cl^\bullet$ system and thermal measurement of the KIEs also indicate that tunneling enhances the reaction probability substantially.[199] A new potential energy surface for this reaction based on an analytical function for the $CH_4 + H^•$ reaction, calibrated by experimental rate coefficients, was proposed.[80] Due to significant secondary isotope effects, the experimental KIEs for chlorination of d_n-methanes vary from $k_H/k_D = 11-16$ (measured for the CH_4/CD_4 system,[200–202] the calculated[80] value is about 13; $k_H/k_D = 12$ was measured for CD_2H_2[203]) to 1.4 (measured[204] for CH_4/CH_3D). The contributions from two partial reactions ($CH_3D + Cl^• \rightarrow DCl + H_3C^•$ and $CH_3D + Cl^• \rightarrow HCl + H_2DC^•$) computed[193] with a dual-level direct dynamics method gave $k_H/k_D = 1.45$ for the $CH_3H(D)\cdots Cl$ contribution. The existing data for the temperature dependence of the KIEs for the CH_4/CD_4 couple were recently analyzed in the 300−1100 K interval.[199]

Numerous dynamics and kinetic studies have been carried out for the chlorination of ethane,[205–207] propane,[208–211] butanes,[208,210,212–214] *n*-pentane,[215] *n*-hexane,[209,210] and some chlorinated hydrocarbons.[216–219] A comprehensive set of kinetic data for the C_2-C_8 hydrocarbons is available together with GC/FID analyses of the reaction mixtures.[220] The calculations of the overall rates for Cl-radical H-abstractions gave $k_{3°}/k_{2°}/k_{1°} = (6.1/8.2/2.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; very similar experimental rate constants $(6.09/8.34/3.32) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} were found by another group.[221] Solvents[222] influence the selectivities of alkane chlorinations significantly. The selectivities in solution relative to the gas phase increase the 3°:1° ratio to 38.0 ± 1.0 for 2,3-dimethylbutane and the 2°:1° ratio for *n*-alkanes to 8.81 ± 0.12 in bromine-containing solvents (CH_3CH_2Br).[223]

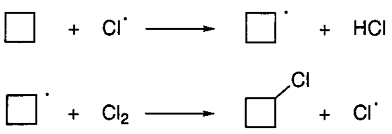
Detailed ab initio calculations for the reactions of chlorine atoms with fluoro- and chloro-substituted methanes and an almost complete analysis of all kinetic data obtained from flash photolysis-resonance fluorescence, discharge flow-mass spectrometry, and competitive photochlorination experiments in the temperature range from 216 to 652 K are available.[224] The activation energies at MP4SDTQ/6-31G(*d,p*), corrected based on bond additivity schemes (BAC-MP4),[225] range from 0.6 kcal mol^{-1} for $CHCl_3$ to 9.7 kcal mol^{-1} for CHF_3. As in the case of methane, tunneling corrections for the chlorination of polyhalomethanes improve the calculated rate constants significantly.[224] G2(MP2) calculations show the best agreement between computed (1.2 kcal mol^{-1}) and experimental (1.5 kcal mol^{-1}) barriers for the H-abstraction with Cl radicals from CH_3F; however, a detailed dynamics analysis shows double-well character of the vibrational adiabatic potential.[226] The same types of potentials were found for $CH_3Cl(Br) + Cl^•$ reactions at the BHandHLYP/6-311G(*d,p*) level.[227] The KIEs for the chlorination of the C−H bonds decrease substantially from 3° to 2° positions. Thus, the KIE for the chlorination of ethane is 3.1[200] (3.08 ± 0.18[228,229]) while it is 1.4 ± 0.2 for *n*-butane[213] and only 1.20 ± 0.06 for cyclohexane.[221]

The C−H abstraction reactions can compete with C−C bond activations in the case of strained hydrocarbons. The differences of the regioselectivities of gas-phase[230,231] and condensed-phase[232] chlorinations of cyclopropane (Scheme 1) were explained[233] by solvent pressure effects. H-Abstraction with the Cl radical from cyclopropane is favorable in the gas phase or in solvents with low internal pressure; solvents with high internal pressure favor S_H2 ring opening (for a recent review on homolytic substitutions, see ref 234). Ring-opening products also dominate in solid-state chlorinations of cyclopropane on amorphous films.[235,236]

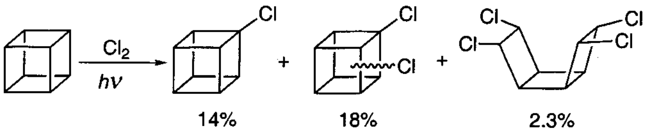
Scheme 1. C−H and C−C Chlorination of Cyclopropane in Different Solvents



Scheme 2. Selective C−H Chlorination of Cyclobutane



Scheme 3. Competitive C−H and C−C Radical Chlorinations of Cubane



In contrast to cyclopropane, the ring opening of cyclobutane by Cl radicals is unfavorable,[237,238] and even in the condensed state,[239] only C−H abstraction takes place (Scheme 2). The addition products are found for highly strained hydrocarbons with weak C−C bonds (like[1.1.1]-[240] and [2.2.2]propellanes[241] and bicyclobutanes[242]).

The photochlorination[243] of cubane with Cl_2/CCl_4 leads to a mixture of chlorocubane and dichlorocubanes as well as to a product from ring opening (Scheme 3).

2.1.3. Bromine Radical

The reactivities of halogen radicals decrease in the direction F > Cl > Br, and in contrast to the transformations of fluorine and chlorine radicals, the $CH_3-H + Br^• \rightarrow CH_3^• + HBr$ reaction is endothermic. Due to the barrierless exothermic formation of hydrogen-bridged complexes ($CH_3^•\cdots H-Br$),[244–246] the reverse reaction is accompanied by a *negative* temperature coefficient (−0.3 ± 0.2),[247] which is even more negative for the *t*-Bu$^•$ + HBr reaction (−1.4 ± 0.2 kcal mol^{-1}).[248]

The C_{3v}-symmetrical TS for the H-abstraction from CH_4 with $Br^•$ (Figure 3) is relatively late (the C−H bond distance is 1.618 Å at MP2/6-31G(*d*)[244] and 1.621 Å at QCISD/311G(2*df,p*)[249]). Similar C−H bond distances were computed for the C−H−Br moieties in the TSs for the reactions of ethane and propane with $Br^•$.[186] The computed QCISD barriers ranges from 16 to 18 kcal mol^{-1} with different basis sets and agree well with experimental values.[250] The differences in the activation energies for the H-abstrac-

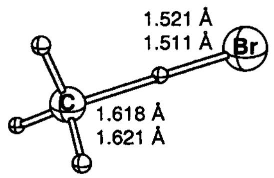
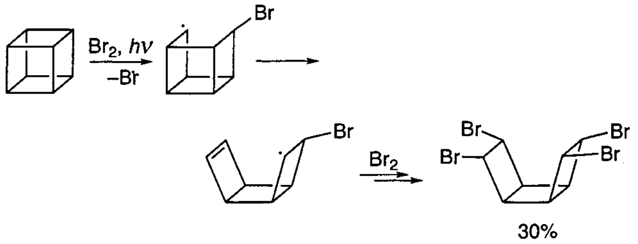


Figure 3. MP2/6-31G(d)[244] and QCISD/6-311G(2df, 2p)[249] optimized geometry of the TS of H-abstraction from methane with the Br radical.

Scheme 4. Ring-Opening Bromination of Cubane



tions from methane (17.5 kcal mol^{-1}),[250,251] ethane (13.0 kcal mol^{-1}),[251,252] propane (9.5 kcal mol^{-1}),[247] and isobutane (6.9 kcal mol^{-1}) render H-abstractions with Br$^{\bullet}$ from methyl groups insignificant when 3° C−H are present in the alkane.[253,254] As the TSs for H-abstraction with the Br radical are more product-like than for the other halogen atoms, the selectivities of radical brominations correlate to some extent with the stabilities of the resulting alkyl radicals. For instance, light-induced radical bromination of adamantane with Br_2 shows a 3°:2° ratio of only 5.7.[255] The experimental data[256] place the almost planar[257] 2-Ad$^{\bullet}$ 2.5 kcal mol^{-1} below 1-Ad$^{\bullet}$; semiempirical[258] as well as B3LYP/6-31G(d) computations, however, suggest that both radicals have almost the same stability.

The influence of halogen substitution on the rates of hydrogen abstraction with the Br radical was studied for the photobromination of halomethanes,[252] CH_3CH_2Cl, CH_3CH_2F,[259] and CH_3CHHal_2.[260] The rate constants for abstractions from the CH_2Hal moiety are higher while those for the methyl group are lower than for ethane. The weakening of the α-C−H bonds arises from the stabilizing resonance interaction of the halogen, facilitating bond cleavage.

The KIEs for alkane brominations in the gas phase and in solution are similar. The value measured for competitive bromination of h_{12}- and d_{12}-cyclohexane in the gas phase is 5.38 ± 0.11 and varies from 5.33 in liquid bromine to 4.30 in highly diluted Br_2/Freon solutions.[261] In contrast to the Cl radical, hydrogen abstractions from strained hydrocarbons are not typical for the Br radical. Ring opening of alkyl-[262,263] and arylcyclopropanes[264,265] with Br radicals occurs regio- and stereoselectively with inversion of configuration (S_H2). The only exception is 9-anthranylcyclopropane where, due to conformational constraints, the C−H bond of the cyclopropane fragment becomes more reactive than the C−C bond.[266] Highly strained cubane reacts with Br radicals exclusively via an S_H2 pathway followed by a second ring opening (Scheme 4).[243]

This reaction was recently studied[267] computationally at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level (Scheme 5). Cubane preferentially undergoes C−H abstraction (pathway ***A***) with the Cl radical (first entries, $\Delta G^{\ddagger}_{298}$ = 4.6 kcal mol^{-1}), while Br radicals open the cage (second entries, $\Delta G^{\ddagger}_{298}$ = 12.0 kcal mol^{-1}). The barrier for the fragmentation ***F*** of the cubane cage with the Br radical is lower than that for the hydrogen-abstraction pathway ***A***. These results nicely agree with the behavior of cubane under radical photochlorination (C−H substitution) and photobromination conditions (cage fragmentation).[243]

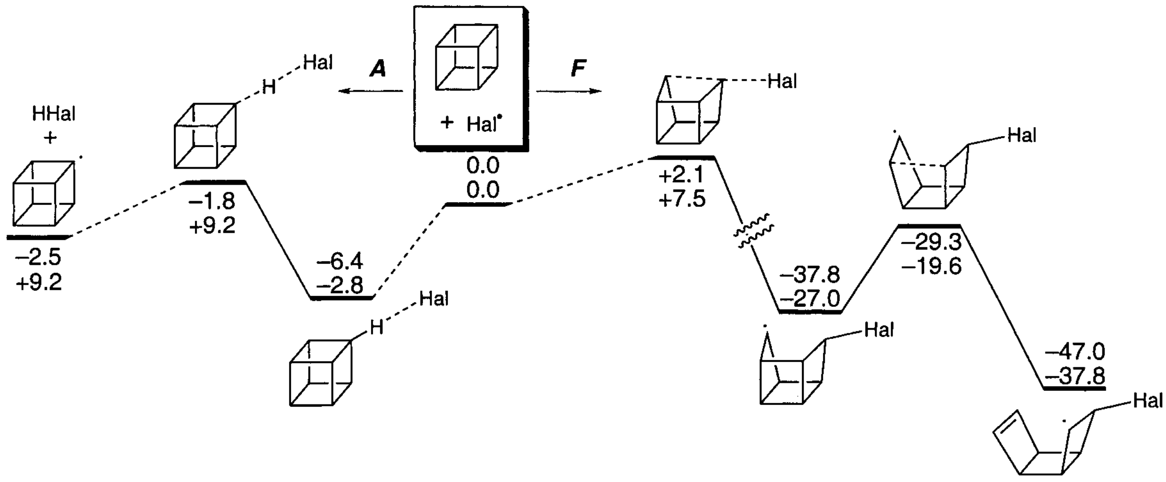
The C−C bonds of strained hydrocarbons can be brominated selectively under radical conditions because of strain relief which singles out certain bonds or molecular moieties. Typical examples are small-ring propellanes,[240,268] bicyclobutanes,[242,269] and bicyclohexanes.[270]

2.2. Oxygen-Centered Radicals

2.2.1. Oxygen

A simplest oxygen-centered triplet (bi)radical, O(^{3}P), abstracts hydrogens in methane combustion: $CH_4 + O(^3P) \rightarrow H_3C^{\bullet} + HO^{\bullet}$.[271] This reaction is computationally challenging due to Jahn−Teller distortion and

Scheme 5. B3LYP/6-311+G(*d*,*p*)//B3LYP/6-31G(*d*) ($\Delta G^{\ddagger}_{298}$, kcal mol^{-1}) Computations on the C−H Abstraction (pathway *A*) vs C−C Addition (pathway *F*) for Cubane with the Cl (first entries) and Br (second entries) Radicals



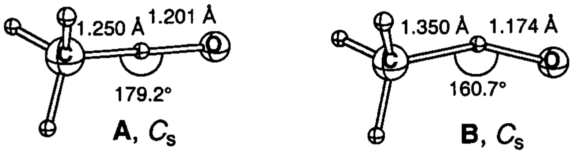


Figure 4. Geometries of the TSs for H-abstraction from methane with $O(^3P)$ (**A**) at MP2/cc-pVTZ)[275] and $O^{\bullet -}$ (**B**) at B3LYP/6-311+G(3*df*,3*pd*).[292]

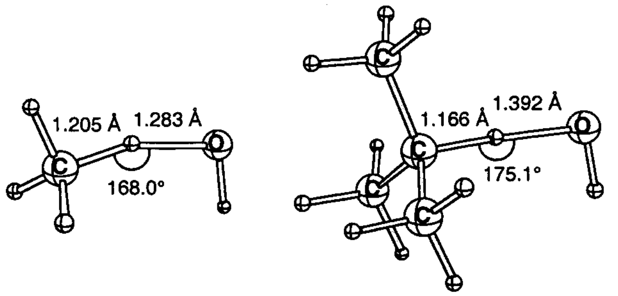


Figure 5. Geometries of the TSs for H-abstraction from methane and isobutane with the OH radical at MP2/6-31G-(*d*,*p*).[304]

splitting of the PES into the $^3A'$ and $^3A''$ manifolds in the activation step. The experimental[272,273] activation energies for the $O(^3P)$ reaction with alkanes, ranging from 7.3 kcal mol^{-1} for 1° to 2.5 kcal mol^{-1} for 3° C−H bonds in the 300−400 K interval,[274] agree well with computations at the MP2/cc-pVTZ level[275] and with the rate constants calculated from the variational transition-state theory with semiclassical transmission coefficients.[276] The TS (Figure 4) has C_s symmetry (with only a small deviation from C_{3v}), and the critical distances are 1.17−1.20 Å (O−H) and 1.25−1.30 Å (H−C). The experimental barriers for $O(^3P)$ reactions with 3°, 2°, and 1° C−H bonds are 3.3, 4.5, and 6.9 kcal mol^{-1}, respectively. The reaction dynamics were studied by laser-induced fluorescence[277,278] and agree well with these values.[274] The low positional selectivity (2°:1° = 1.3) ratio was estimated by experimental studies on the $O(^3P) + C_3H_8$ branching reaction.[279] Reactions of halogenated alkanes with the $O(^3P)$ are especially important for atmospheric chemistry and have been computed recently for CHF_3 and a number of fluoromethanes.[280,281]

Another simple oxygen radical, the $O^{\bullet -}$ radical anion, which is held responsible for the oxidation of hydrocarbons on metal oxide surfaces,[282−288] has a large hydrogen-atom affinity and high basicity.[289] The reactions with alkanes proceed (for $CH_4 + O^{\bullet -}$ reaction dynamics, see ref 290) via two different channels: hydrogen abstraction (to give $OH^- + Alk^\bullet$) and reactive detachment (yielding $H_2O + e^- +$ alkene).[291] The H-abstraction TS (Figure 4) for the $CH_4 + O^{\bullet -}$ reaction is nonlinear (∠O−H−C = 160.7°), and the B3LYP/6-311+G(3*df*,3*pd*) barrier is 6.8 kcal mol^{-1}.[292] The experimental kinetics show a negative temperature dependence ($T^{-0.3\pm 0.15}$)[293] as the formation of an initial complex $[O\cdots CH_4]^{\bullet -}$ is substantially exothermic (−5.9 kcal mol^{-1} at B3LYP/6-311+G(3*df*,3*pd*).[292]

2.2.2. Hydroxy Radical $HO^\bullet$

The reaction of saturated hydrocarbons with the OH radical, which is one of the most important radicals in atmospheric[52,55,294] and combustion[295] chemistry, also plays a central role in many biological processes.[296]

An enormous number of papers describe computations on the $CH_4 + HO^\bullet$ system, trying to reproduce the experimental activation energy (3.6 kcal mol^{-1} at 298 K) and rate constant (0.789×10^{-14} cm^3 molecule^{-1} s^{-1}).[297,298] B88, G1,[299] CI,[97] MP−SAC2,[300,301] QCISD[302,303] and G2[304] methods overestimate while the B3PW91,[305] BLYP,[306] and B3LYP[307] approaches underestimate the barrier by 1−2 kcal mol^{-1}. Multireference MP methods reproduce the barrier heights better.[100] The $CH_4\cdots OH^\bullet$ complex which influences the experimental barriers and KIEs was identified through electron spectroscopy.[308] Canonical transition-state theory with multidimensional semiclassical tunneling corrections (CVT/SCT)[300] reproduces the experimental values and the curvature of the temperature dependence of the rate constants. The CVT description of the adiabatic profile with multidimensional tunneling (MT) direct dynamics calculations show that an adiabatic reaction maximum lies between the CCSD(T)-SAC//MP2/cc-pVTZ (5.6 kcal mol^{-1}) and CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ (6.2 kcal mol^{-1}) values, and a proper description of the profile is crucial for estimating tunneling corrections.[309] Recent computations[310] based on the canonical unified statistical model using a microcanonical optimized multidimensional tunneling approach (CUS/μOMT) reproduce the experimental barrier exactly but underestimate the experimental KIEs for this reaction (measured as 7.36 ± 0.88 for CH_4/CD_4, 3.30 ± 0.50 for CH_4/CHD_3, 1.81 ± 0.28 for CH_4/CH_2D_2, and 1.25 ± 0.14 for CH_4/CH_3D around 300 K).[311]

The barriers for H-abstraction correlate strongly with the exothermicities of the reaction of small alkanes with the OH radical ($\Delta H_r = -14.4, -18.2, -20.7$, and -22.8 kcal mol^{-1} for methane, ethane, propane, and isobutane)[60] and correlate with the stabilities of the radicals thus formed.[60,312,313] MP2/6-31G(*d*,*p*) computations for methane and the 1°, 2°, and 3° C−H bonds of the above hydrocarbons show that the more exothermic the reaction is, the earlier the TS is located on the PES. In the TS for the $CH_4 + HO^\bullet$ reaction, the C···H distance is 1.205 Å, while it is 1.166 Å for $(CH_3)_3C{-}H + HO^\bullet$ (Figure 5). The opposite is observed for the newly formed H−O bond, which is the shortest for $CH_3\cdots H\cdots OH$ (1.283 Å) and the longest for $(CH_3)_3C\cdots H\cdots OH$ (1.392 Å).[304] The geometrical changes in the TSs reflect the KIEs ($k_H/k_D = 4.6$,[314] 2.6,[315] and 1.9[316] for abstraction from 1°, 2°, and 3° C−H bonds). However, dual-level (DL) dynamics computations of the rate constants for the reaction of propane with $HO^\bullet$ show that the experimentally measured KIEs are dominated by tunneling effects.[317] The H/D KIEs for the reaction with OH radicals in the gas phase are 2.59 ± 0.16[315,318] for cyclohexane and 2.74 ± 0.17 for cyclopentane.[315] Similar reactivities and KIEs were found for cyclohexane and cyclopentane recently in solution for the OH radical generated from peroxonitrous acid.[319] Generally, the KIEs for H-abstraction with OH radicals are slightly higher than those for abstractions with the Cl radical.[81]

The substantial differences in the barriers for 1°, 2°, and 3° H-abstractions with the OH radical lead to largely different experimental rate constants[320,321] (average values are 0.243×10^{-12}, 1.11×10^{-12}, and 2.06×10^{-12} for ethane, propane, and isobutane at 298 K, respectively).[322] A comprehensive analysis of the existent literature data together with the latest rate constants for reaction of the 10 C_2-C_6 linear and C_5-C_8 cyclic alkanes with the OH radical show that most of the rate constants are now known to better than 5% accuracy over the 300−400 K temperature range.[323]

The rate constants for the reactions of OH radicals with cyclopropane and cyclobutane (1.11×10^{-13} and 17.5×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K) were measured[324] with laser flash photolysis/resonance fluorescence techniques. The relative reactivities of the CH_2 groups in cyclic alkanes with OH radicals gave the following statistically corrected values: 0.37 for c-C_3H_6, 4.4 for c-C_4H_8, 10.0 for c-C_5H_{10}, 11.9 for c-C_6H_{12}, and 16.9 for c-C_7H_{14}. The temperature dependence of a set of rate constants for the reactions of $HO^\bullet$ with a number of linear and cyclic C_4-C_6 alkanes was analyzed recently.[325]

Fenton-type Reagents. The mechanisms for alkane activation with Fenton-like reagents (H_2O_2/ML_x, M = Fe, Cu, Co, Mn; L = H_2O and others) are discussed intensively in the literature[326] (for the most recent and detailed review, see ref 327). There is evidence for[328,329] and against[330−333] the participation of HO radicals in the alkane activation step (eq 2).

$$M^{n+1} + H_2O_2 \rightarrow MOH^n + HO^\bullet \tag{1}$$

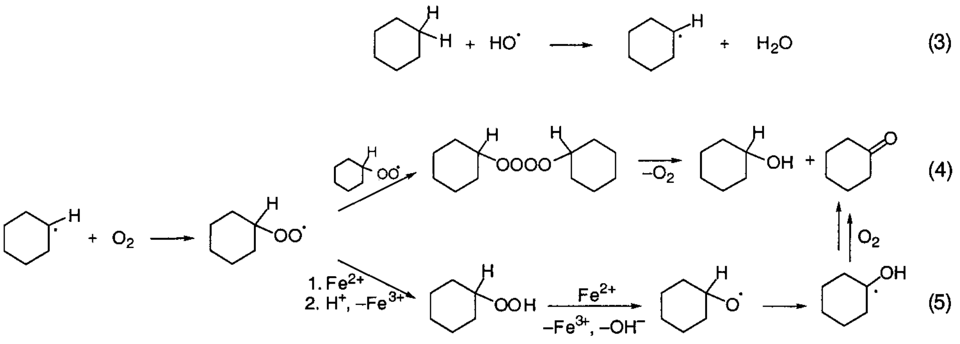
$$R-H + HO^\bullet \rightarrow R^\bullet + H_2O \tag{2}$$

Indeed, “*...mechanisms of Fenton-like processes are extremely complex, and it is not surprising that different conclusions* [...] *were reached for different reagents and substrates*”.[334] Recent studies[335] of the oxidation of cyclohexane (KIE = 1.5−2.7) and adamantane (3°:2° = 3.1−3.3) with $[FeL(CH_3CN)](ClO_4)_2/H_2O_2$ suggested the involvement of $Fe^{IV}=O$ species as “*...a more selective oxidizing species in addition to hydroxy radicals*”.

Peculiar secondary over tertiary[336,337] selectivities (for instance the 2°/3° ratios up to 22 for adamantane) observed for alkane oxidations under Gif conditions ($Fe/pyridine/CH_3COOH/O_2(H_2O_2)$)[338,339] initially were a strong argument against a radical activation step; a nonradical scheme based on the participation of high-valent iron−oxo species was proposed instead.[330] However, the importance of $OH^\bullet$ in the C−H activations in Gif conditions was pointed out already at the beginning of 1990s.[340] Some analogies between Gif and Fenton chemistries were first drawn[341] but then rejected[342,343] on the basis that free 2-Ad$^\bullet$ radicals are not formed in Gif systems because 2-adamantyl pyridine trapping products could not be identified. However, it was shown independently that 2-Ad$^\bullet$ simply cannot react with pyridinium ions under these conditions.[344] At the same time, trapping with TEMPO gave substantial amounts of 2-adamantyl-TEMPO.[345] The oxidation of adamantane is one of the most controversial aspects of Gif chemistry,[346] and the mechanism indeed seems rather complex. Numerous follow-up mechanistic studies were undertaken in an attempt to support nonradical activation through Fe(V)=O or Fe(IV)=O[347] species in Gif systems based on the competitive reactivities of cycloalkanes,[348,349] trapping of possibly formed iron−carbon bond intermediates,[350,351] investigations of the role of solvent,[352] and using alternative peroxide sources.[353] However, mechanistic reinvestigations[354] and recent adamantane oxidations[355,356] under Gif conditions, support the intermediate formation of diffusively free 1-Ad$^\bullet$ and 2-Ad$^\bullet$. Careful and complete analysis[355] of the reaction mixtures in adamantane oxidations including non-oxygenated[357] products shows that a 3°:2° ratio of 2−4 is close to that observed for the oxidations of adamantane with $HO^\bullet$ in non-Gif systems. The lack of intermolecular selectivity[358] also confirms that HO radicals are involved in the activation step (eq 3). The relatively large amounts of ketones vs alcohols formed in Gif systems[359] might be explained in terms of the traditional Haber−Weiss−Walling[328] mechanism proposed for Fenton-like chemistry (eq 4) when decomposition of *sec*-peroxyradicals $R_2CHOO^\bullet$ may take place also “*...via metal-dependent pathways*” and 1,2-H shifts (eq 5).[355]

The halogenation selectivities of Gif systems with halomethanes as halogen sources certainly are different[360] from halogenations with the same reactant in the presence of traditional radical starters, but oxygen-containing products still form, and these make mechanistic interpretations difficult. Moreover, the selectivities for the formation of halogen products in Gif systems differ from the oxygen-containing product distributions.[355] Alkanes are oxidized in solution with Gif-like H_2O_2/catalyst systems such as $O_2-H_2O_2-$vanadium[361−363] or H_2O_2-manganese complexes.[364] The oxidations of n-pentane, n-hexane, and adamantane with Keggin-type iron complexes again show inverse selectivities, i.e., 2° > 3° > 1° (vide infra).[365]

The kinetics and energetics of hydrogen abstractions with $HO^\bullet$ from halogenated hydrocarbons have been the subject of many investigations. The reaction of the OH radical with HCF_3 is about 2 orders of magnitude slower than with methane. The 9.6 kcal mol^{-1} barrier for the $HO^\bullet + HCF_3$ reaction was computed at the QCISD/6-311G(d,p)//MP2/6-311G(d,p) level;[366] recent studies estimate the classical barrier height as 2.8−3.1 kcal mol^{-1}.[367] An entire set of $CH_{4-n}F_n + HO^\bullet$ reactions was studied with MP2[368] and DFT[369] methods, which, however, generally underestimate the barriers; at the same time, surprisingly, MP2/6-31G(d)//HF/3-21G(d)[370] provides reasonable barriers, probably due to favorable error cancellation. Recently, a modified G2 study showed the best agreement with the experimental values both for fluoromethanes and for methane itself.[371] It is important to note that a second fluorine influences the H-abstraction barriers only slightly. A number of other haloalkane + $OH^\bullet$ reactions were studied experimentally and computationally at correlated levels.[372−379] A satisfactory correlation ($R = 0.93$) has been observed between the activation energies and



the C−H bond dissociation enthalpies for halomethanes and haloethanes[62] as well as between ab initio computed rate constants and those estimated with the empirical Evans−Polanyi equation.[379]

The selective oxidation of methane to methanol as an alternative fuel prompted a detailed study of the $CH_3OH + HO^•$ reaction.[380] The overall rate constant[381] both for the $CH_3O^• + H_2O$ and the $^•CH_2OH + H_2O$ channels is $9.1-9.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, but the abstraction from the methyl group dominates[382] (the barrier[383] is only 0.9 kcal mol^{-1}). However, selective methane oxidation with HO radicals could be achieved in catalytic systems such as H_2O_2/Keggin-type heteropolyacids[384] or in the presence of vanadium complexes.[385] The most effective approach is the direct oxidation of methane to methanol by soluble methane monooxygenase (MMO),[386] which is believed to occur without the involvement of *free* HO radicals (vide infra).

2.2.3. Haloxy Radicals HalO•

Despite their importance for combustion chemistry, very little is known about the reactivity of haloxy radicals with alkanes. The kinetics of the $ClO^•$ [387] and $BrO^•$ [388] as well as computations for $FO^•$ [389] reactions with CH_4 are available; the first detailed computational study for the whole set of the $HalO^• + CH_4 \rightarrow HalOH + CH_3^•$ reactions was performed only recently[390] at the MP2, QCISD(T),[249] and B3LYP levels with several basis sets. The computed barriers are 11.2, 15.3, and 13.9 kcal mol^{-1} for $FO^•$, $ClO^•$, and $BrO^•$ reacting with methane at B3LYP/cc-pVTZ//B3LYP/6-311G(*d*,*p*), respectively (for the geometries of the TSs, see Figure 6).

2.2.4. Alkoxyl Radicals RO•

Studies of alkoxy radicals in alkane activations frequently focus on the *t*-BuO radical. A competition between H-abstraction and β-scission is usually observed for *t*-BuO• and depends on solvent polarity and hydrogen-bonding ability.[391] The TS for H-abstraction from methane with the *t*-BuO• was recently[392] computed at B3LYP/6-31G(*d*); the C−H distance in this nonlinear TS is 1.145 Å, and the computed H/D semiclassical KIE = 6.46. The chemistry of this radical in the condensed phase was studied in detail. *t*-BuOCl homolysis (eq 6) leads to alkane chlorinations with *t*-BuO• as the H-abstractor (eq 7), but the Cl radical can also activate alkanes (eq 8).

$$t\text{-BuOCl} \rightarrow t\text{-BuO}^• + \text{Cl}^• \qquad (6)$$

$$\text{R}-\text{H} + t\text{-BuO}^• \rightarrow \text{R}^• + t\text{-BuOH} \qquad (7)$$

$$\text{R}-\text{H} + \text{Cl}^• \rightarrow \text{R}^• + \text{HCl} \qquad (8)$$

This makes kinetic measurements with the hypochlorite technique[393,394] unreliable, and "*the studies using the tert-butyl hypochlorite technique cannot expected to be very accurate*".[395] Laser photolysis of *t*-BuO−N=N−OBu-*t* or *t*-BuO−OBu-*t*[395,396] produced "pure" *t*-BuO radicals for kinetic measurements. The most recent kinetics[397] gave rate constants of 9.8×10^5 and 7.2×10^5 M^{-1} s^{-1} for cyclohexane ($E_a = 3.49$ kcal mol^{-1}) and cyclopentane ($E_a = 3.54$ kcal mol^{-1}) for the reaction with *t*-BuO• in PhF. In general, the solvent has only a moderate influence on the kinetic parameters of these reactions.[395,398−401] The C−H selectivities reported for *t*-BuO• in the reactions with a number of linear as well as branched[402] alkanes are $k_{2°}/k_{1°} = 12$[403] and $k_{3°}/k_{1°} = 50$,[404] i.e., these are quite high relative to those of OH, Cl, and Br radicals. The chlorination of adamantane with *t*-BuOOBu-*t* in $CHCl_3$ gave a 1-AdCl/2-AdCl ratio of 10:1.5.[255] This is one of the most selective adamantane radical chlorination reactions studied to date (vide infra, however).

t-BuOCl can also be used for the chlorinations of the C−H bonds of strained hydrocarbons, because C−C bonds remain untouched in the presence of the *t*-BuO radical[405] even in cubane.[406] Similarly, the incorporation of iodine into unactivated C−H bonds is based on the homolysis of in situ generated *t*-BuOI in the presence of alkanes.[407] The *t*-BuO• recently received some attention as a model for the reactions of cytochrome P450[408,409] (vide infra) and alkane hydroxylation mechanisms with alkylhydroperoxides in the presence of transition-metal complexes.[410,411]

The *t*-BuO radicals are likely to be active species in the oxidations of alkanes with *t*-BuOOH under Fe catalysis, which initially was attributed to a non-radical process promoted by a high-valent iron−oxo species. It was recognized from the kinetics and product distributions that radical activation certainly occurs at high *t*-BuOOH concentrations.[7,412] The constant ratio (2.0−2.2:1) for hydrogen-atom abstractions from *c*-C_8H_{16} and *c*-C_6H_{12} and similar H/D KIEs (4.8−4.9) for the *c*-C_8H_{16}/*c*-C_8D_{16} couple with *t*-BuOOH/$[Fe^{III}_2(TPA)_2(H_2O)_2]^{4+}$ and *t*-BuON=NOBu-*t* support

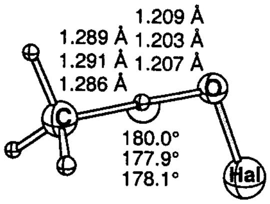


Figure 6. Geometries of the TSs for H-abstractions from methane with $FO^•$ (first entry), $ClO^•$ (second entry), and $BrO^•$ (third entry) at QCISD/6-311G(*d,p*).[390]

a common R−H + t-$BuO^•$ activation step.[359] Other systems based on iron complexes such as $[FeL](ClO_4)_n$/t-BuOOH,[413,414] $[Fe_2L(OH)](BF_4)_3$/t-BuOOH,[415] $[Fe_2OL_2(H_2O)_2](ClO_4)_4$/$t$-BuOOH,[416] and $[FeL(Cl_2)]BF_4$/t-BuOOH[417] can also produce t-$BuO^•$; however, the KIEs for the c-C_6H_{12}/c-C_6D_{12} couple are sometimes higher ($k_H/k_D = 10$[416] for $[Fe_2OL_2(H_2O)_2](ClO_4)_4$/$t$-BuOOH) than with t-$BuO^•$, indicating a more complex reaction scheme probably involving alkylperoxo-iron(III) species.[416] Still, "*the possibility of a free radical pathway operating simultaneously cannot be ruled out*".[418] Fenton-like chemistry based on (ML_x, M = Fe, Cu, Co, Mn, Ru)/t-BuOOH systems[329,418−424] probably involves radical chain reactions including the t-$BuO^•$ + R−H activation step. An analogous situation in alkane oxidations takes place when t-$BuO^•$ is produced from the homolytic cleavage of complexes such as $[Co(Py_3P)OOR]$, R = t-Bu[425] or others.[426] These systems demonstrate "normal" selectivities for adamantane oxidations, independent of R (3°:2° = 10−12). Similar (3°:2° ≈ 8−13) selectivities for low-yield adamantane oxidations were reported for some ferrous oxo/peroxo pivalate[427] for a number of Cu(I),[428] Ti(IV),[429] and Keggin-type[430] complexes with t-BuOOH. The selectivities for adamantane oxidations with t-BuOOH in the presence of the transition-metal cation-exchanged fluorotetrasylilic mica[431] and μ-oxa-bridged diferric complexes[432] are 3°:2° = 9−12, probably also due to the t-$BuO^•$ involvement in the activation step. Similar selectivities were obtained for adamantane brominations (3°:2° ≈ 8−10) for Gif, Mn-porphyrin, Fe-porphyrin/t-BuOOH/$BrCCl_3$ systems;[433] these are similar also for alkane oxidations catalyzed by other Fe,[357] Fe_2,[434−436] Ru,[437,438] Co,[439] and Cr complexes[440] in the presence of t-BuOOH. Diiron non-heme MMO model precatalysts also lent themselves as t-$BuO^•$-producing species.[441] Methyl cubanes yield only cage-substituted products[243] with t-$BuO^•$; oxidations with MMO or P450 give different product distributions[408] and KIEs.[442] An extensive discussion concerning the participation of oxygen-centered radicals[341,433,443−445] vs Fe(II)=O/Fe(IV)=O and Fe(III)=O/Fe(V)=O C−H activations[343,348,446−449] in alkane functionalizations with ROOH under Gif-like conditions performed by a number of groups recently reached an agreement[411,450] regarding the decisive role of radical chain reactions initiated by t-$BuO^•$.

In summary, it is very probable that most (if not all) metal-catalyzed t-BuOOH alkane activations involve the same t-$BuO^•$ + R−H activation step and not the alternative M=O + R−H reaction. It has been recommended that "*...all investigators who would like to claim that t-butyl hydroperoxide-derived high-valent metal-oxo species are the effective oxidizing agents in their systems to check...*" whether they will "*...yield the same results as t-butyl hydroperoxide before they draw any mechanistic conclusions*".[410] A recent review[451] on biomimetic non-heme iron catalysts for alkane hydroxylations shows that "*with ROOH as oxidant, it is clear from mechanistic studies that alkoxyl radicals are the principal agents that cleave the alkane C−H bond...*". The metal is involved in the post-activation step by means of trapping and/or oxidizing the carbon-centered radicals. Moderate enantioselectivities observed in some of these reactions might be explained by the fact that the carbon-centered radicals formed after the H-abstraction step are not free and can recombine quickly. The enantioselective recombination of prochiral carbon-centered radicals also cannot be excluded.[452,453]

Alkane halogenations are more selective in Gif systems which can be explained by a combination of free-radical and redox processes.[341] It was shown[443] that Gif conditions could be more effective than Fenton chemistry for the chlorination of cyclohexane in the presence of Cl^- (eq 9), because the low steady-state concentration of Fe(II) minimizes the reduction (eq 10) of t-$BuO^•$, which is probably also the H-abstracting reagent in such systems (eq 11).

$$c\text{-}C_6H_{11}^{\bullet} + Fe(III){-}Cl \rightarrow c\text{-}C_6H_{11}Cl + Fe(II) \tag{9}$$

$$t\text{-}BuO^{\bullet} + Fe(II) + H^+ \rightarrow t\text{-}BuOH + Fe(III) \tag{10}$$

$$c\text{-}C_6H_{12} + t\text{-}BuO^{\bullet} \rightarrow c\text{-}C_6H_{11}^{\bullet} + \text{t-BuOH} \tag{11}$$

Halogen substitution enhances the reactivity of the alkoxyl radicals substantially. The changes in the rate constants (298 K, cm^3 $molecule^{-1}$ s^{-1}) in the reaction of $CF_3O^•$ with methane ($1.93 \pm 0.11 \times 10^{-14}$), ethane ($1.30 \pm 0.11 \times 10^{-12}$), propane ($4.84 \pm 0.27 \times 10^{-12}$), and isobutane ($6.73 \pm 0.39 \times 10^{-12}$)[454] are very similar to those found for the HO radical.[322] Among other radicals of this type, the cumyloxyl kinetics with cyclohexane are available.[455]

2.2.5. Peroxy Radicals $ROO^•$

Although it was recognized that under Gif conditions "t-butylperoxide radicals do not abstract hydrogen from saturated hydrocarbons",[450] the rate constants for a number of H-abstractions from linear, branched, and cyclic alkanes with t-$BuOO^•$ generated in the t-BuOOH/AIBN system were studied by competitive kinetics and fall in the range from 1×10^{-4} to 9×10^{-4} M^{-1} s^{-1} for 2° C−H bonds. The reactivities of the 3° C−H bonds are higher (from 1×10^{-3} to 2×10^{-2} M^{-1} s^{-1}) depending on the structure of the alkane.[456] The activation energies for 3° and 2° C−H bonds were found in the range 13−19 kcal mol^{-1}.[457] In general, the reactivity of t-$BuOO^•$ with C−H bonds is 7−10 orders of magnitude lower than that of t-$BuO^•$,[458,459] as the H−O BDE in t-BuOOH[460] is only 88.2 vs 105.2 kcal mol^{-1} of that in t-BuOH.[264] t-BuOO radicals, possibly together with t-$BuO^•$, are present in Kharasch oxidations with t-BuOOH/$Cu(OAc)_2$[461] and in metalloporphyrin-catalyzed decompositions of t-BuOOH.[462] The selectivities for C−H abstraction from adamantane with these reagents are almost identical (3°:2° = 27–28); they also show similar relative reactivities with different hydrocarbons, and it was noted that "*also in this oxidation t-BuOO$^\bullet$ is the hydrogen abstracting species*" and that the "*...intermolecular selectivities would be rather complex*".[462]

The involvement of aroylperoxyl radicals ArC(O)-OO$^\bullet$ was recently proposed for the oxidation of alkanes with peracids.[463] Despite the fact that the O–H bond in ArC(O)OOH is ca.17 kcal mol^{-1} weaker than the one in ArC(O)OH, effective H-abstraction with ArC(O)OO$^\bullet$ *can* take place due to its high electrophilicity. Previously proposed[464] ArC(O)O$^\bullet$ H-abstractions or concerted oxygen insertions[465] into C–H bonds do not seem to be operative.

2.2.6. Aroyloxyl Radicals ArC(O)O$^\bullet$

These radicals may form under homolysis of aromatic peracids ArC(O)OOH or aroylperoxides ArC-(O)OO(O)CAr and are able to abstract hydrogens from saturated hydrocarbons ($k = 1.2 \pm 0.4 \times 10^7$ M^{-1} s^{-1} for 4-$ClC_6H_4C(O)O^{\bullet}$ [466] and $5.3 \pm 3 \times 10^5$ M^{-1} s^{-1} for 4-$CH_3OC_6H_4C(O)O^{\bullet}$ [467] with cyclohexane), but this process competes with decarboxylation ArC(O)-O$^\bullet$ → Ar$^\bullet$ + CO_2. Initially mechanisms involving a Ar$^\bullet$ + R–H activation step were initially proposed[468] but ruled out later.[463] The yields and selectivities of hydrocarbon azidations[469,470] and amidations[471] carried by stabilized ArC(O)O radicals are high (3°:2° > 60 for adamantane). An exceptionally high selectivity for the oxidation of adamantane (3°:2° = 140) by *m*-CPBA was observed in benzene[463] and explained by the participation of aroylperoxyl radicals ArC(O)OO$^\bullet$ in the C–H activation step followed by different reaction paths (eqs 13 and 14),[472] e.g., through a non-chain radical mechanism.

$$\mathrm{ArC(O)O^{\bullet} + ArC(O)OOH \rightarrow ArC(O)OH + ArC(O)OO^{\bullet}} \quad (12)$$

$$\mathrm{ArC(O)OO^{\bullet} + H{-}R \rightarrow ArC(O)O^{\bullet} + ROH} \quad (13)$$

$$\mathrm{ArC(O)OO^{\bullet} + H{-}R \rightarrow ArC(O)OR + HO^{\bullet}} \quad (14)$$

However, such high 3°/2° selectivities are not typical for a radical attack on the C–H bonds of adamantane and are more consistent with a highly polar oxygen rebound mechanism (vide infra). The latter is also consistent with the observed partial stereoselectivity of C–H oxygenation at tertiary carbon atoms with CH_3COOOH.[473] The positional selectivities for the oxidation of adamantane and a number of other hydrocarbons with CF_3COOOH are even higher.[474,475]

2.2.7. $NO_x^{\bullet}$ Radicals

The NO_x radicals contribute substantially to the atmospheric degradation of hydrocarbons,[52] especially at night-time ($NO_3^{\bullet}$).[56] As the oxidation of methane with O_2 is accelerated by the addition of NO$^\bullet$,[476,477] which also increases the selectivity for CH_2O formation, the CH_4/NO$^\bullet$ and $CH_4/NO_2^{\bullet}$ systems were studied in detail. CCSD(T)/6-311++G(2*d*,*p*)//MP2/6-311++G(2*d*,*p*) calculations[478] show two possible channels for the CH_4 + NO$^\bullet$ reaction due to the ambient nature of the NO radical, i.e., through $(ON\cdots H\cdots CH_3)^{\ddagger}$ and $(NO\cdots H\cdots CH_3)^{\ddagger}$ transition structures (the barriers are 61.7 and 72.0 kcal mol^{-1}, respectively). The barriers for the reaction of CH_4 with $NO_2^{\bullet}$ [479] are much lower: 33.4 kcal mol^{-1} for $(O_2N\cdots H\cdots CH_3)^{\ddagger}$ and 41.1 kcal mol^{-1} for (*trans*-$ONO\cdots H\cdots CH_3)^{\ddagger}$ at CCSD(T)/6-311++G(2*d*,*p*)//MP2/6-311++G(2*d*,*p*).[478] The $\Delta H^{\ddagger}$ values at CCSD(T)/6-311++G(2*d*,*p*)//BHandHLYP/6-311G(*d*,*p*) are 34.3 and 36.2 kcal mol^{-1}, respectively; however, recent computations[480] showed that the (*cis*-$HONO\cdots H\cdots CH_3)^{\ddagger}$ channel has the lowest barrier (31.0 kcal mol^{-1} at BHandHLYP/6-311G(*d*,*p*), Figure 7).

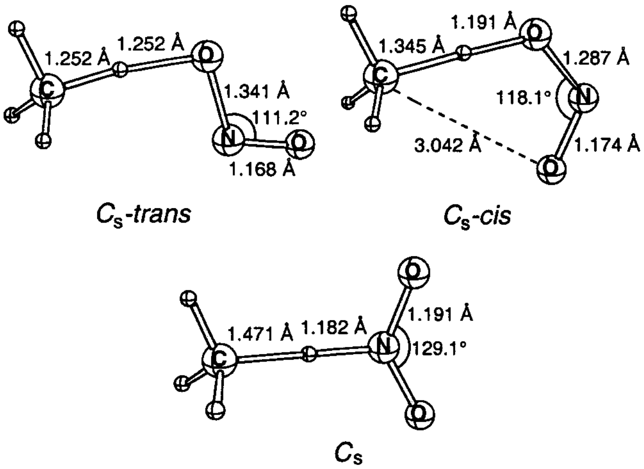
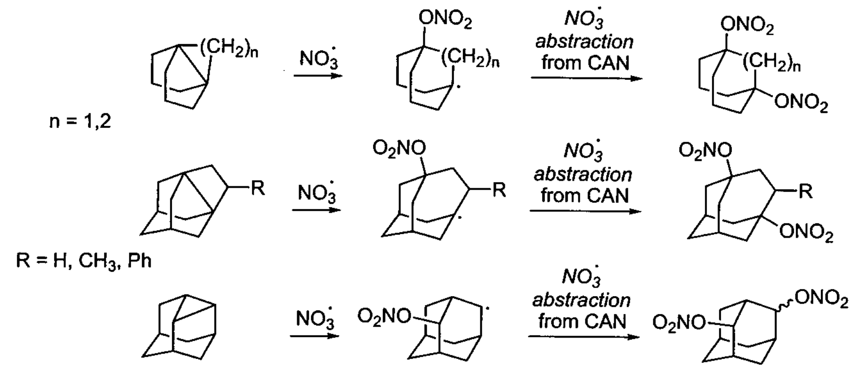


Figure 7. TSs for H-abstraction from methane with the NO_2 radical at BHandHLYP/6-311G(*d*,*p*).[480]

A decrease in the barrier was computed for the H-abstraction from the 1°, 2°, and 3° positions of small alkanes with $NO_2^{\bullet}$. The lowest barrier is 20.8 kcal mol^{-1} for the 3° C–H bond of isobutane through the *cis*-TS. These results indicate that $NO_2^{\bullet}$ can participate in alkane oxidations with O_2 in the presence of nitrogen oxides.[478,481]

The reactivity of $NO_2^{\bullet}$ is substantially increased in the presence of ozone (Kyodai-nitration[482]), where highly reactive[483] NO_3 radicals[484] form. The reaction rates for hydrogen abstraction from alkanes with NO_3 radicals are about 10^{-17} cm^3 molecule^{-1} s^{-1}.[485–487] A more convenient way to generate $NO_3^{\bullet}$ is the photodecomposition of cerium(IV) ammonium nitrate (CAN).[488] In the photoinduced reaction of adamantane with CAN, an unprecedented high selectivity (3°:2° = 60) for a radical functionalization reaction was observed.[489] The 3° selectivities for adamantane in the Kyodai NO_2/O_3 system are almost the same (>50).[490] The activation energy (3.2 kcal mol^{-1}) for the reaction of adamantane with the NO_3 radical was computed at AM1.[491] The exceptionally high selectivities for H-abstractions were explained by the high electrophilicity of $NO_3^{\bullet}$ and the "*radical cationic nature of the transition state*".[491] The NO_3 radical is also able to cleave saturated C–C bonds in strained compounds. The barrier computed recently for S_H2 ring opening of 1,1-dimethylcylopropane with $NO_3^{\bullet}$ (Figure 8) is only 3.6 kcal mol^{-1} at B3LYP/6-311+G-(*d*,*p*)//B3LYP/6-31G(*d*).[492] The dinitroxylations of the

Scheme 6. C−C Bond Activations with the NO_3 radical



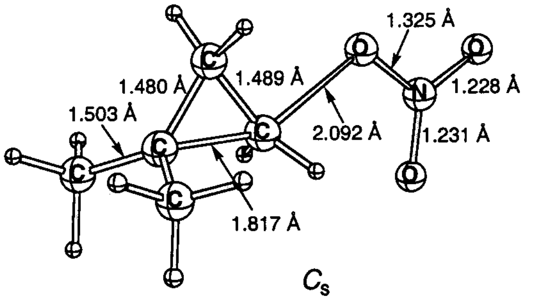
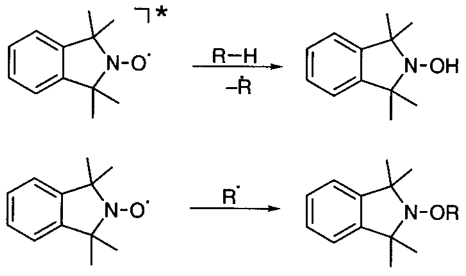


Figure 8. Transition structure for the attack of the NO_3 radical on the carbon atom of 1,1-dimethylcyclopropane at B3LYP/6-31G(*d*).[492]

Scheme 7. C−H Activation with Photoexcited Nitroxide



C−C bonds of propellanes occur with high selectivities and do not compete with C−H activation (Scheme 6).[492]

High selectivities (3°:2°:1° = 50−60:7:1) were reported for other highly electrophilic radicals such as nitroso oxides $X{=}N{-}O^{\bullet}$.[493] Nitroxides $R_2N{-}O^{\bullet}$ in their ground states are quite stable radical species and are not able to react with the C−H bonds. Photoexcited 1,1,3,3-tetramethalisoindolin-1-yloxyl and some other nitroxide reagents, however, are able to abstract hydrogens from unactivated C−H bonds regioselectively.[494] The resulting alkyl radicals are efficiently trapped by ground-state nitroxide (Scheme 7). The preparative yield for cyclohexane substitution is 77% and 55% for *n*-butane (2°:1° selectivity = 6.7).

The *phthalimide-N-oxyl* (PINO) radical[495,496] can easily be generated from *N*-hydroxyphthalimide in the presence of molecular oxygen with[497,498] or without[499] catalyst. Using PINO as the H-abstracting radical allows the transformation of alkanes to alcohols, ketones, and carboxylic acids. The selectivities for the adamantane oxidations are quite high, and the 1-hydroxyadamantane/adamantan-2-one ratios vary from 80/5 to 40/14.[500] Similar selectivities were observed for PINO-initiated carboxylations of adamantane in the CO/O_2 system.[499] Catalytic amounts of *N*-hydroxyphthalimide promote the oxidation of cyclohexane with NO_2 radicals to give 70% nitrocyclohexane[501] and adamantane to 1-nitroadamantane in nitric acid (yield 62%, 3°/2° = 22).[502] PINO is a chain carrier radical in isobutane in the selective aerobic oxidation to *tert*-butyl alcohol.[498]

Photoexcited quinones and ketones act as efficient but unselective H-abstractors. The triplet state of 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranyl) abstracts hydrogens with rates from 0.8×10^6 to 2×10^6 M^{-1} s^{-1}, and hydrocarbon radicals thus formed may be oxidized further by this reagent.[503] The selectivity for the chlorination of adamantane by photoexcited chloranyl is very low (3°:2° = 7).[503] Similarly low selectivities were observed for photoinduced hydrogen abstraction from adamantane by triplet states of aromatic ketones ($Ar_2C{=}O$).[504] Among the other oxidizing/H-abstracting reagents, the $SO_4^{\bullet-}$ radical anion[505] should be mentioned as it is quite useful for the activation of unreactive hydrocarbons.[506−508]

2.3. Nitrogen-Centered Radicals

NH_2 Radical. The barrier for the hydrogen-abstraction reaction $NH_2^{\bullet} + CH_4 \rightarrow NH_3 + H_3C^{\bullet}$ was computed by a number of groups as 17.1 kcal mol^{-1} at CI/6-31G//HF/6-31G,[509] 14.8 kcal mol^{-1} at MP2/6-311++G(2*d*,*p*)[510] as well as at QCISD(T)/6-311+G-(2*df*,2*p*)//QCISD/6-311G(*d*,*p*),[511] 14.9 kcal mol^{-1} at CCSD(T)/6-311++G(2*d*,*p*)//MP2/6-311++G(2*d*,*p*),[510] 12.3 kcal mol^{-1} at PMP2/6-311++G(2*d*,*p*),[510] about 15 kcal mol^{-1} with different G2 approaches,[512,513] and 10.8 kcal mol^{-1} at B3LYP//6-311+G(2*d*,*p*).[510] The experimental value is "$>$10 kcal mol^{-1}" in the temperature interval from 300 to 500 K.[514] As the above reaction is only 2−3 kcal mol^{-1} exothermic, the TS is located about halfway along the reaction path (the critical C−H and H−N bond distances are 1.33 and 1.26 Å in the nearly linear N−H−C fragment, Figure 9).[512,513]

A systematic study of the reactions of small alkanes with the NH_2 radical was performed with a modified G2 method giving barriers of 11−12 (11.3 via MP2/6-311+G(*d*,*p*)[515]), 8.4, and 8.3 kcal mol^{-1} for 1°, 2°, and 3° C−H activations, respectively.[513] This is in agreement with the experimental trends;[516−518] how-

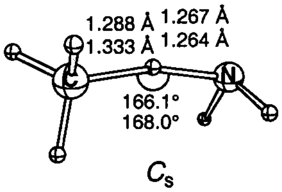


Figure 9. Transition structure for H-abstraction from methane with the NH_2 radical at QCISD (first line)[511] and B3LYP (second line)[512,513] with the 6-311G(*d*,*p*) basis set.

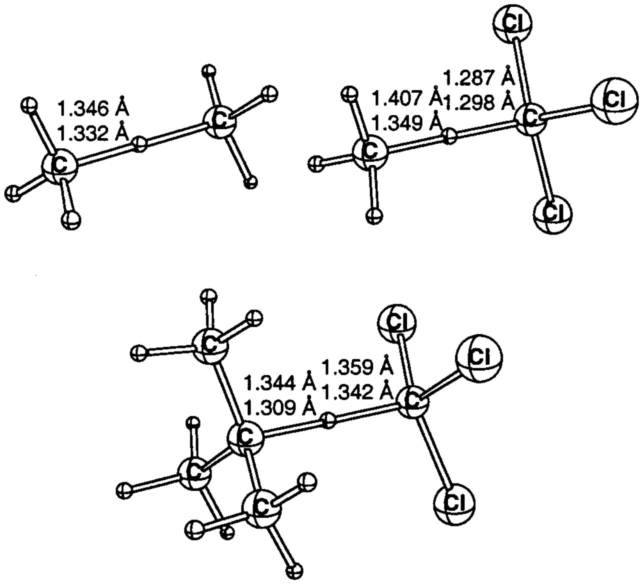
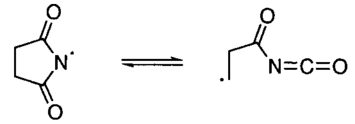


Figure 10. Transition structures for the H-abstraction from methane and isobutane with methyl and chloromethyl radicals: B3LYP/6-31G(*d*) (first entry), MP2/6-31G(*d*) (second entry).[532,553]

Scheme 8. Two Forms of Succinimidyl Radical



ever, the computed barrier for the 3° abstraction probably is overestimated: the selectivities determined by amination reactions of 2,2- and 2,3-dimethylbutane, methylcyclohexane, and *n*-hexane with $H_2N^•$ gave 3°:2°:1° = 70:7:1.[519]

NBS as a source for the *succinimidyl radical* is traditionally used as a radical starter for free-radical brominations. It was recognized that this radical is less selective in H-abstracting than the bromine radical.[520] When adamantane is brominated with Br_2 under photoinitiation the 3°:2° ratio is 5.7, while it is only 4.3 with NBS.[255,521] There was a long-standing discussion about the mechanism of action of succinimidyl radicals,[522] which can exist in a dynamic equilibrium with its ring-opened isomer (Scheme 8),[523] that influences the H-abstraction selectivities.[524]

The selectivities for alkane activations with *amidyl radicals* were studied in detail for the chlorination of hydrocarbons with *N*-chloroamides.[525] The selectivities of the amidyl radicals $CH_3C(O)N^•R$ markedly depends on the size of R: the 3°:1° selectivity is 95 for R = CH_3 but only 1.6 for R = *t*-Bu. In general, the selectivities for chlorination with *N*-chloroamides are higher than with elementary chlorine (3°:2° = 35 for adamantane; free-radical chlorination with Cl_2 gave 3°:2° = 1.9 only[526]).

The selectivities for the Minisci chlorination[433,527–529] initiated by $R_2NH^{•+}$ *radical cations* generated from *N*-chloroamines in acidic media is strongly influenced by polar effects. High selectivities were found for the chlorination of adamantane under these conditions (3°:2° = 32) due to the high positive charge on the hydrocarbon moiety of the TS (eq 15).[344]

$$\mathrm{Ad{-}H} + \mathrm{R_2NH^{\bullet+}} \rightarrow [\mathrm{Ad{\cdots}H{\cdots}NHR_2}]^{\bullet+\ddagger} \rightarrow \mathrm{Ad^\bullet} + \mathrm{R_2NH_2}^+ \quad (15)$$

2.4. Carbon-Centered Radicals

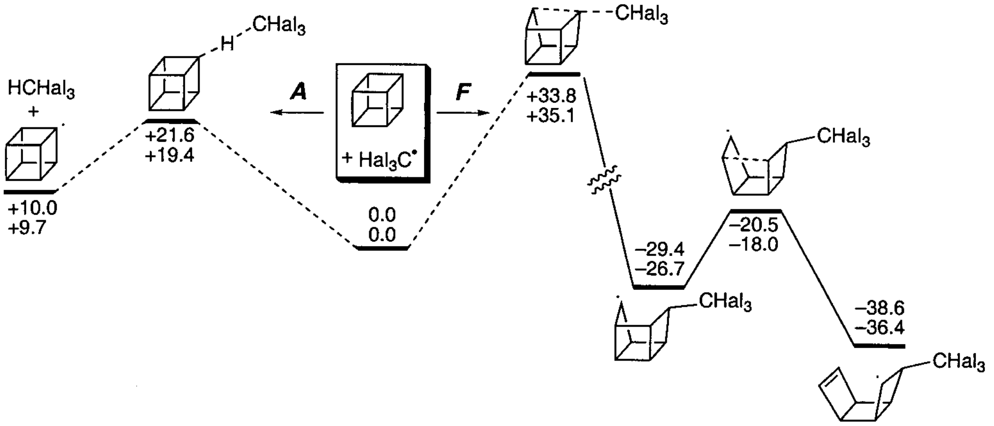
The barrier for the thermoneutral CH_4 + $H_3C^•$ reaction was computed first at noncorrelated[530] then at MP2[531] levels: both methods overestimate the barrier by about 4–5 kcal mol^{-1}; B3LYP and B3P86 with different basis sets[532] give values close to experiment[533] (14.1 kcal mol^{-1}); tunneling probabilities were estimated using CI[534] and MP4/6-311G(*d*,*p*)[535] potentials. The critical C–H bond distances in the D_{3d}-symmetrical TS are similar at all levels of theory (from 1.33 to 1.34 Å) (Figure 10). The KIE value reported for CH_4/CD_4 ranges from 3.8 to 4.6[536] and is computed as 3.2.[537]

The kinetics of the reaction of small alkanes with methyl radicals were evaluated at moderate to combustion temperatures, and the relative 3°:2°:1° reactivities were estimated as 61:4.8:1 at 350 K.[538] This agrees with the trend in the experimental[539] activation energies (11.0, 12.5, and 13.2 kcal mol^{-1}, respectively). The influence of chloro/fluoro substitution on the reaction of methane with methyl radicals was studied computationally at MP2/6-31G(*d*,*p*)//HF/6-31G(*d*,*p*).[540] The exothermicities of the $H_3C^•$ + $CH_{4-x}Cl_x$ → CH_4 + $^•CH_{3-x}Cl_x$ reactions strongly depend on *x* and are much higher for $CHCl_3$ (−9.1 kcal mol^{-1}) than for CH_3Cl (−4.4 kcal mol^{-1}). As a consequence, the activation energy is the lowest for $CHCl_3$ (calculated = 7.1 kcal mol^{-1} and experimental[541] = 6.7 kcal mol^{-1}) among chloromethanes (10.2, 9.0 kcal mol^{-1} for CH_2Cl_2 and 14.4, 11.6 kcal mol^{-1} for CH_3Cl). In contrast, all $H_3C^•$ + $CH_{4-x}F_x$ → CH_4 + $^•CH_{3-x}F_x$ reactions are more exothermic (−10 to −11 kcal mol^{-1}) but the barriers for H-abstraction are similar (computed are 14–16 kcal mol^{-1}, experimental[542] range = 10–12 kcal mol^{-1}).

Due to the higher stabilities and hence relatively high selectivities, halosubstituted ($Cl_3C^•$, $Br_3C^•$, $F_{2n+1}C_n^•$) alkyl radicals are widely used for alkane activations. They can be generated by thermolysis,[543] photolysis with[544] or without TiO_2,[545] or transition-metal-catalyzed[433,546–548] as well as reductive decomposition of halomethanes with alkali metals[549] or under phase-transfer catalytic (PTC) conditions (vide infra).

The reactions of $^•CCl_3$, produced from CCl_4 homolysis were studied in detail. It is generally accepted that this reaction involves initiation (eq 16), activa-

Scheme 9. B3LYP/6-311+G(*d,p*)//B3LYP/6-31G(*d*) ($\Delta G^{\ddagger}_{298}$, kcal mol^{-1}) Computations on the C−H Abstraction (pathway *A*) vs C−C Addition (pathway *F*) for Cubane with the CCl_3 (first entries) and CBr_3 (second entries) Radicals



tion (eq 17), propagation (eq 18), and termination (eq 19) steps.

$$CCl_4 \rightarrow {}^{\bullet}CCl_3 + {}^{\bullet}Cl \qquad (16)$$

$$R{-}H + {}^{\bullet}CCl_3 \rightarrow R^{\bullet} + CHCl_3 \qquad (17)$$

$$R^{\bullet} + CCl_4 \rightarrow R{-}Cl + {}^{\bullet}CCl_3 \qquad (18)$$

$$2{}^{\bullet}CCl_3 \rightarrow Cl_3C{-}CCl_3 \text{ or } 2R^{\bullet} \rightarrow R_2 \qquad (19)$$

The rate constants for eq 17 measured in solution[550] are very similar to those in the gas phase,[551,552] in contrast to the rates of the propagation step (eq 18) which is 2−3 orders of magnitude faster in solution. The initiation depends somewhat on the nature of the radical starter (AIBN, *t*-BuOOBu-*t*, or $BrCCl_3$). In the latter case, however, the initiation process does not provide a clean source of $Cl_3C^{\bullet}$.[550] The activation energies for H-abstraction changes dramatically from methane (17.9 kcal mol^{-1}), ethane (14.2 kcal mol^{-1}), propane (10.6 kcal mol^{-1}), to isobutane (7.7 kcal mol^{-1}).[551] Computations at the HF level give unsatisfactory results; the MP2 and B3LYP methods with different basis sets overestimate the barriers by about 3 and 2 kcal mol^{-1}, respectively; pure DFT (BLYP) gives barriers almost identical to experiment.[553] All computations show linear (Alk)C···H···CCl_3 configurations in the TSs (Figure 10) with a shortening of the C···H and an elongation of the H···CCl_3 distances when going from methane to the 3° C−H bond of isobutane. The role of polar contributions in the TS is relatively small and was estimated for the halogenations of substituted toluenes with the Cl_3C radical ($\rho(\sigma+) = -0.69$).[554]

Pronounced 3° C−H selectivities were found for chlorinations with the Cl_3C radical, which is much more selective than the Cl radical and most other free-radical chlorinating agents.[555] Consequently, the 3°:2° reactivities of adamantane toward the Cl_3C radical is 24.[556−558] In the absence of Cl radicals (using more easily homolyzable $BrCCl_3$ as the Cl_3C-radical source), the selectivity for the adamantane chlorination is even higher (3°:2° = 27.0). Recently, CCl_4 was used for the chlorination[267] of hydrocarbons in the presence of NaOH under phase-transfer (PT) conditions, where formation of $Cl_3C^{\bullet}$ results from the reduction of tetrachloromethane with HO^{-} [267,559] (eq 20, Hal = Cl) and decomposition (eq 21, Hal = Cl) of the $CCl_4^{\bullet -}$ radical anion (dissociative electron transfer).[560]

$$CHal_4 + OH^{-} \rightarrow CHal_4^{\bullet -} + HO^{\bullet} \qquad (20)$$

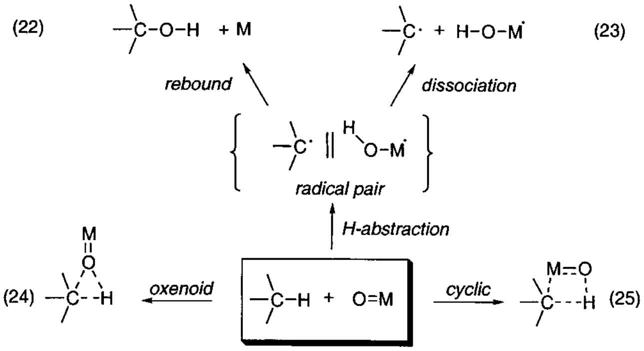
$$CHal_4^{\bullet -} \rightarrow {}^{\bullet}CHal_3 + Hal^{-} \qquad (21)$$

Such an initiation avoids the formation of Cl radicals and is most useful for the clean chlorination of strained compounds such as cubane.[267] In marked contrast to free-radical halogenations with Hal_2, which cause fragmentation of the cubane skeleton, PT halogenations do give the desired halocubanes *without* cage fragmentation. Computations at B3LYP/6-311+G(*d,p*)//B3LYP/6-31G(*d,p*) show that the barriers for the H-abstraction (Path ***A***, Scheme 9) with $CHal_3$ radicals (Hal = Cl, first entry, Hal = Br, second entry) are much lower than those for direct carbon attack (fragmentation path ***F***).[267]

More easily homolyzable tetrabromomethane (CBr_4) as a source of $Br_3C^{\bullet}$ is quite often used as a selective brominating agent.[544,546] Recently, a new preparative PT method for the bromination of hydrocarbons was introduced, again involving eqs 20 and 21, with Hal = Br. The PTC-brominations in the CBr_4/NaOH/PT-catalytic system were applied to a wide range of hydrocarbons (linear and (poly)cyclic alkanes).[561] Participation of the CBr_3 radical in the activation step of the PT brominations was demonstrated by the excellent agreement of computed KIEs with the experimental values ($k_H/k_D = 4{-}5$).[562] The PT method was used also for direct iodination of unactivated hydrocarbons in the HCI_3/NaOH system.[563] Due to sterically more demanding *CI_3 radical*, the selectivities for C−H activations are even higher (3°:2° = 120 for adamantane iodination) than with CBr_3 radicals.

The *CF_3 radical* can be generated by thermal decomposition of CF_3COOOH, where a radical chain process dominates in the reaction with cyclohexane at 70 °C. The participation of ${}^{\bullet}CF_3$ in the activation step $c\text{-}C_6H_{12} + F_3C^{\bullet} \rightarrow c\text{-}C_6H_{11}^{\bullet} + HCF_3$ was proven by the detection of fluoroform (or DCF_3 with C_6D_{12})

Scheme 10. Possible Mechanisms for Alkane Activations with Metal−Oxo Species



in the course of the reaction.[564] Perfluorinated alkyl radicals[565,566] are more reactive toward C−H abstraction than alkyl radicals. Ethane effectively reacts with $^\bullet CF_3$ generated from the radical-initiated thermolysis of perfluoroacetic acid anhydride.[567] Competitive kinetics were used for the reaction of the n-$C_4F_9CF_2CF_2$, n-C_4F_9, and i-C_3F_7 radicals with alkanes and haloalkanes.[568] With cyclohexane, the i-C_3F_7 radicals are 5.6 times more reactive than n-$C_4F_9^\bullet$, which are ca. 2 orders of magnitude more reactive than n-$C_4H_9^\bullet$. The 2°:1° selectivities (about 12) of n-$C_4F_9^\bullet$ measured for its reaction with n-heptane are somewhat higher than those for the t-BuO radical.[394] The relatively high selectivities for perfluorinated alkyl vs alkyl radicals were explained by polar and electrostatic effects.[568] The iodinations of alkanes with $R_fI/t\text{-}BuOOH/CH_3COOH$ by a free-radical chain process carried by $R_f^\bullet$ was described.[569,570] However, the 3°:2° selectivity for the iodination of adamantane[569] with n-C_4F_9I, where primary n-C_4F_9 radicals are involved in the activation step, is considerably lower than halogenations of adamantane initiated by tertiary haloalkyl radicals such as CI_3[563] or CBr_3.[561] The k_H/k_D KIE for H-abstraction from cyclohexane with perfluorinated branched α-keto radicals is high (3.45),[571] which is typical for carbon-centered radicals. Other carbon-centered radicals such as vinyl,[572] CN,[573] ethynyl,[574] and phenyl[134,575−577] radicals are not as commonly used for alkane activations.

3. Formation of Alkane Radicals with Nonradical Reagents

$$\mathbf{R{-}H + X \rightarrow R^\bullet + H{-}X^\bullet}$$

Formation of two open-shell molecules from two closed-shell reactants is quite rare, and such reactions are classified as "molecule-assisted (induced) homolysis".[578] These types of mechanisms were postulated for alkane activations with metal−oxo reagents M=O (Scheme 10). These reactions are almost thermoneutral or only slightly exothermic because the newly formed H−O bond is strong and the lowering of the high-valent state of the metal to $H{-}O{-}M^\bullet$ provides extra stability. The radical pair thus formed can recombine ("rebound", eq 22) or escape from the solvent cage to give free radicals ("homolysis", eq 23).

The mechanistic interpretations of alkane activations with neutral closed-shell reagents (stable metal−oxo species, cytochromes, peracids, dioxiranes, etc.) are vividly debated. Difficulties arise from alternative possibilities for concerted insertions of the M=O reagents into the C−H bonds (oxenoid insertion, eq 24)[117] and concerted cycloadditions (eq 25),[10,11] where the same products could form without the formation of radical pairs. Herein we discuss only the radical pathways which are most consistent with the available experimental and computational data.

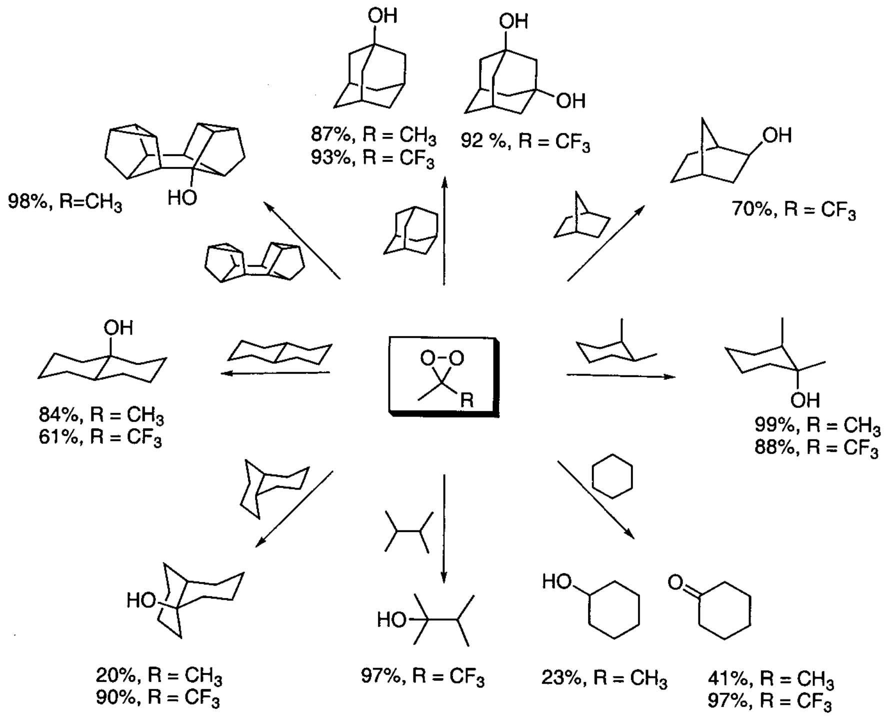
3.1. Dioxiranes

Dioxiranes (three-membered cyclic peroxides) are now widely used for the oxidation of various classes of organic compounds,[579−581] but most remarkable is the reactivity of these peroxides toward saturated hydrocarbons. Dimethyldioxirane (DMD),[582] methyl(trifluoromethyl) dioxirane,[583,584] and their nitrogen analogues—oxaziridines[585]—are employed for hydrocarbon oxidations under mild conditions with high preparative yields, and impressive stereoselectivities. Generated in situ from a ketone and oxone, DMD shows high oxyfunctionalization selectivities.[586] Exceptionally high selectivities for the hydroxylation of cyclohexane, adamantane,[582,583] Binor-S,[582] 2,3-dimethylbutane,[584] stereoisomeric 1,2-dimethylcyclohexanes, as well as decalines[584,587] were observed (Scheme 11) also for methyl(trifluoromethyl)dioxirane, and very similar results were obtained for hydrocarbon functionalizations with oxaziridines.[585,588] The selective oxidation of the C−H bonds in strained compounds[589] by DMD is possible even in the presence of the cyclopropyl group.[582,590] The C−H bond insertions generally are stereoselective with retention of configuration.[591,592]

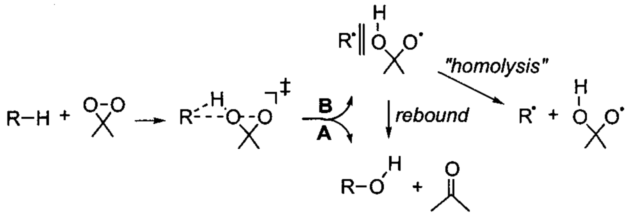
There are a number of mechanistic studies on the C−H activations with dioxiranes.[593−595] Difficulties arise from free-radical side reactions:[593,594,596,597] clean second-order kinetics are observed only in the absence of oxygen (273 K: $k_2 = 2.9 \times 10^{-2}$ M^{-1} s^{-1}, $\Delta H^\ddagger = 13.7$ kcal mol^{-1} and KIE = 2 for the reaction of cyclohexane with methyl(trifluoromethyl)dioxirane).[598] However, it was pointed out that "*...a concerted oxenoid mechanism is kinetically hard to distinguish from a stepwise process with intermediate fast-collapsing caged radical pairs (oxygen rebound)*".[591] The KIEs are generally higher for oxidations with DMD ($k_H/k_D = 6$ in acetone and 3.6 for the gas-phase oxidations of cyclohexane).[599] The KIE for the oxidation of cyclododecane vs d_{24}-cyclododecane[587] is 4.97. The strong electrophilic nature of the oxidizer is evident from the good correlation with the Taft constants ($\rho_I = -2.39$) for the hydroxylations of substituted adamantanes.[600,601] A number of studies support a concerted oxenoid insertion[591,594,598] and the radical rebound/molecule induced homolytic[593,596,599,602−604] C−H bond cleavage. Radical clocks gave unrearranged products and are more consistent with concerted oxenoid insertion.[605,606]

A more detailed mechanistic picture for the C−H activation with dioxiranes was drawn with the help of a number of high-level computations. Structural studies, energetics for decomposition pathways,[607−610] and transition structure optimizations for the activa-

Scheme 11. Alkane Functionalizations with Dimethyl and Methyltrifluoromethyl Dioxiranes



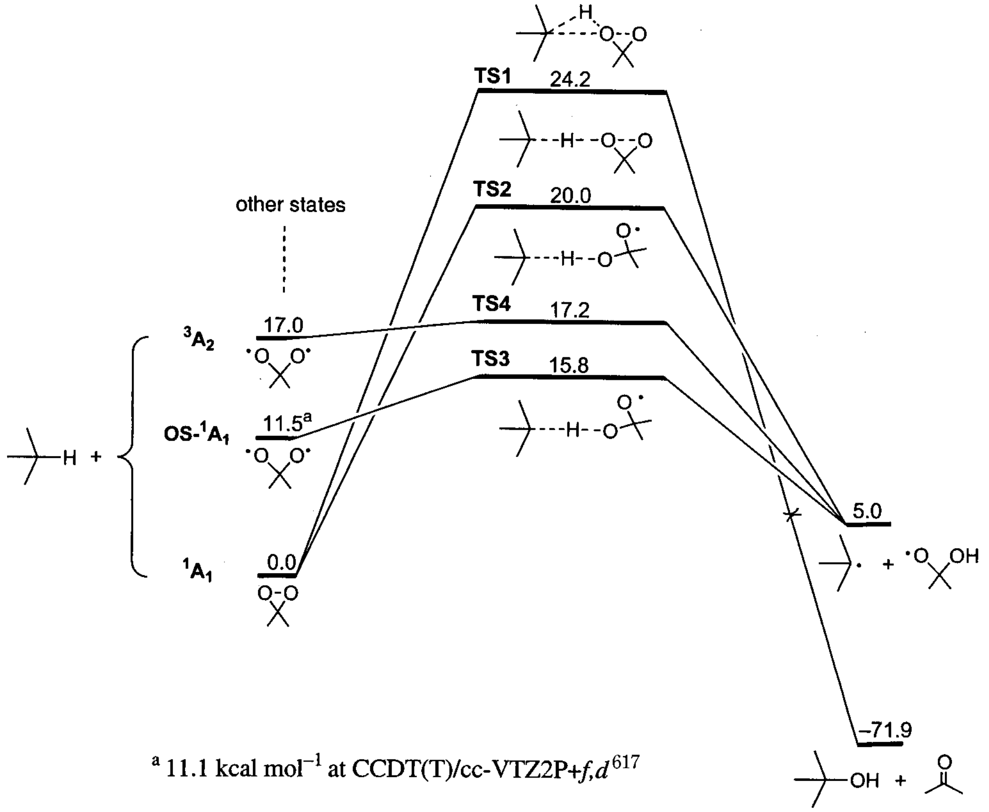
Scheme 12. Bifurcation of the Reaction Path for the C−H Activation Step with Dimethyldioxirane



tion step were performed. The activation energies for model cyano-substituted dioxirane reactions with methane, ethane, the 2° C−H bond of propane, and the 3 °C−H bond of isobutane at the B3LYP/6-31G(*d*) level are 35.0, 27.1, 19.8, and 14.2 kcal mol^{-1}, respectively.[611] For unsubstituted dioxirane, the barriers are slightly higher at the same level (45.8, 36.1, and 32.0 kcal mol^{-1} for methane, ethane, and the 3° position of the isobutane) but decrease substantially at the CCSD(T)/6-31G(*d*)//B3LYP/6-31G(*d*) and B3LYP/6-311+G(3*df*,2*p*) levels.[612] Calculations with unrestricted wave functions decrease the barriers slightly, indicating some biradical character of the transition state. The IRC procedure applied to the TSs revealed that "*no distinct radical intermediates or second transition structures were found*", i.e., concerted insertion is favorable.[612] Consequently, a re-interpretation of the oxidation mechanism, reconciling contradictory experimental data, was proposed,[613] and a number of puzzling and controversial experimental results first were rationalized[613] in terms of a bifurcation of the reaction path (Scheme 12) which involves either concerted insertion (**A**) giving hydroxy products directly[591] or a radical pair (**B**) via a common transition structure. The bifurcation point is located about 2 kcal mol^{-1} below and after the TS. This was supported both by an IRC calculation procedure and, independently, by a restricted bond distance geometry optimization of the radical pair. Radical pairs thus formed either recombine (rebound)[602] or escape from the solvent cage, giving rise to free radicals (molecule-induced homolysis).[593] Interestingly, such reaction paths were previously intuitively predicted by experimentalists, namely, that after a slow step the "*alternative to direct collapse into products—some radical character develops*"[594] or "*cage radical pairs are formed after the slow step*".[591]

The mechanistic dichotomy in the reactions of DMD with alkanes also may arise from the potential multistate reactivity[614] of DMD. The closed-shell $^1A_1$ singlet ground state is only 11.5 kcal mol^{-1} more stable than the biradical open-shell OS-$^1A_1$ singlet state at B3LYP/6-311+G(*d,p*)//B3LYP/6-31G(*d*) (11.1 kcal mol^{-1} at CCSD(T)/cc-VTZ2P+*f,d*).[615] Computations show that three distinctly different pathways on the singlet PES could take place as shown in Scheme 13 for the reaction of DMD with isobutane. Insertion of $^1A_1$-DMD into a C−H bond occurs in a concerted fashion (**TS1**) as found by a number of groups.[267,611,612,616] The barrier for this reaction at B3LYP/6-311+G(*d,p*)//B3LYP/6-31G(*d*) is 24.2 kcal mol^{-1}. The H-abstraction via linear **TS2** with formation of the radical pair exemplifies the molecule-induced homolytic pathway.[616] While it is accompanied by a lower barrier (20.0 kcal mol^{-1}), this reaction is endothermic. The barrier for the radical reaction with OS-$^1A_1$-DMD is even lower (**TS3**, 15.8 kcal mol^{-1}) and may also lead to radical pair formation, although this pathway is hampered by the high barrier for DMD homolysis (the O−O bond breaking requires an activation of 23.0 kcal mol^{-1} at CCSD(T)/cc-VTZ2P+*f,d*,[615] and 23.1 kcal mol^{-1} at B3LYP/6-31G(*d,p*)).[615] H-Abstraction can also occur on the ground-state triplet surface: the $^3A_2$-DMD biradical lies 5.5 kcal mol^{-1} above the OS-$^1A_1$ singlet, and

Scheme 13. B3LYP/6-311+G(*d*,*p*)//B3LYP/6-31G(*d*) (ΔE, kcal mol^{-1}) Computations on the C−H Activation with the Different Electronic States of Dimethyl Dioxirane[67]



[a] 11.1 kcal mol^{-1} at CCDT(T)/cc-VTZ2P+*f*,*d*[617]

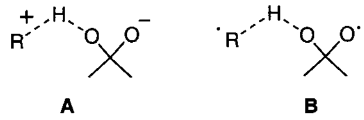
H-abstraction with $^3A_2$-DMD via **TS4** forming the radical pair is virtually barrierless.[267,617]

Dioxiranes are also characterized by a number of low-lying exited states[609] which may participate in the C−H activation reactions; these channels are supported by recent observation of (albeit faint) chemiluminescence in the reaction of dioxiranes with hydrocarbons.[618] Thus, the activation of C−H bonds with DMD is indeed very complex: traces of radical starters may cause free-radical processes and, depending on the reaction media as well as the structure of the hydrocarbon, different reaction pathways may be followed. Hypersensitive radical clocks with rearrangement times close to the lifetime of the transition states[591,605] do not support free-radical pathways but leave the question of a concerted vs molecule-induced homolytic/rebound mechanism unanswered.[267] A concerted mechanism certainly is more favorable as only very weak σ-bonds, like the C−C bond in highly strained 1,3-dehydroadamantane,[617] can be homolyzed by ground-state singlet DMD. The C−C bond in less strained housane has already remained untouched and only concerted C−H oxidation takes place.[619]

The polar nature of the TSs (structure A) with a cationic carbon (the net charge on the CH_3 fragment is +0.124e) and some diradical character (structure B) is a possible explanation for the exceptionally high 3° selectivities found in functionalizations with dioxiranes,[613] which proceed under moderate ET control (as a superposition of structures A and B, Scheme 14).

Similar transition structures for the C−H bond activations of methane, ethane, propane, and isobutane were computed recently for peroxynitrous acid.[620] However, the energy of the ONO−OH bond homolysis is low,[621] supporting the notion that, in contrast to earlier suggestions,[622] HO radicals are responsible for the C−H activation step.

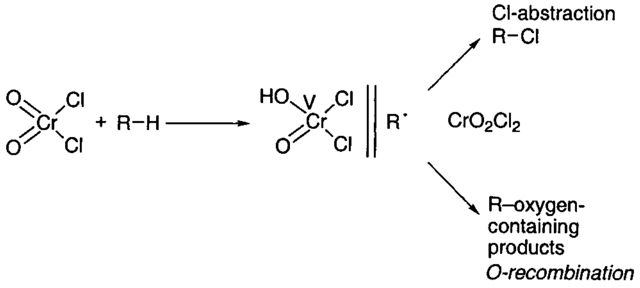
Scheme 14. Polar Contributions in the Transition Structure for C−H Activation with Dimethyldioxirane



3.2. Stable Metal−Oxo Reagents

High-valent metal−oxo compounds such as CrO_3, $KMnO_4$, OsO_4, RuO_4, and others are powerful and very popular oxidants in preparative (hydrocarbon) chemistry. Two distinctly different mechanisms could be operative: radical H-abstraction[623] and 2 + 2 cycloaddition.[624] Mechanistically the most well-studied is the reactivity of covalent chromyl−oxo reagents CrO_2Y_2 (Y = Cl, OAc, O_2CCF_3) which are soluble in organic solvents. The chemistry of chromyl−oxo reagents has been developing since the oxidation reaction was discovered very early by Étard.[625] The reactivities of chromyl−oxo reagents toward alkanes are quite high (*n*-hexane is oxidized by $CrO_2(O_2CCF_3)_2$ to give a mixture of hexanones at −50 °C[626]), but the selectivities for the oxidations of linear, branched, and cyclic[627,628] alkanes are usually low. The oxidations of polycyclic cage compounds[629] are more selective, giving predominantly tertiary-sub-

Scheme 15. Molecule-Induced Homolysis of C−H Bonds with CrO_2Cl_2

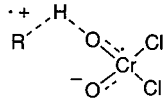


stituted products and ketones (3°:2° = 24 for the $Cr(O_2OAc)_2$[630] and almost completely regiospecific for the $CrO_2(O_2CCF_3)_2$[626] oxidation of adamantane). The mechanisms of chromyl−oxo reactions with alkanes based on product distributions[631] and the nature of the CrO−H bond[632] were studied in detail for CrO_2Cl_2.[623,633−636] These studies provide rationalizations for the driving force of the reaction (the formation of a strong MO−H bond) and confirm the initial suggestion[637] that the rate-limiting step in C−H bond activations by metal−oxo reagents involves H-radical abstraction ($M^n{=}O + H{-}R \rightarrow M^{n-1}{-}OH + R^\bullet$).

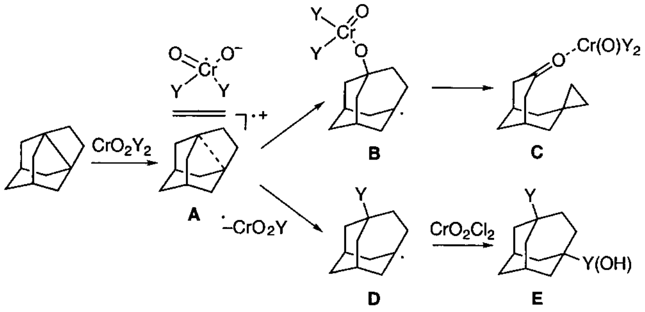
Condensed-phase kinetics for the oxidation of cyclohexane[634] gave second-order rate constant with $k_2^{340} = 1.07 \times 10^{-5}\ M^{-1}\ s^{-1}$ and $\Delta H^\ddagger = 26.6$ kcal mol^{-1} for the activation step; the reactivity of the 2° position of c-C_8H_{16} ($k_2^{340} = 1.86 \times 10^{-5}\ M^{-1}\ s^{-1}$) and the 3° C−H bond of i-BuH ($k_2^{340} = 2.33 \times 10^{-5}\ M^{-1}\ s^{-1}$) is higher.[635] In general, there are good correlations for the rate constants and the KIEs ($k_H/k_D = 2.2{-}2.3$) for the H-abstraction by CrO_2Cl_2 and oxygen-centered radicals. The hydrocarbon radicals formed after the H-abstraction (Scheme 15) are trapped by the CrO_2Cl_2 without a barrier ($k_2 = 1.07 \times 10^9\ M^{-1}\ s^{-1}$), and the overall process occurs as a non-chain radical reaction (Scheme 15). Radical trapping leads to chlorides or Cr^V−alkoxides which are well-characterized[638] and form alcohols after aqueous workup. The intermediacy of carbon-centered radicals $R^\bullet$ was shown by trapping experiments with $CBrCl_3$[634] and by the rearrangements of radical clocks (oxidation of isopropylcylopropane with the CrO_2Cl_2).[636]

The driving force and the nature of the transition structures for the H-abstraction with the Cr=O species are of great interest.[639] The formation of a relatively strong H−O bond (80−85 kcal mol^{-1}) in $HOCr^V(O)Cl_2$ together with the reduction of the $Cr^{VI} \rightarrow Cr^V$ makes the overall reaction favorable. A particularly important observation was made: "*Since the proton portion of the hydrogen atom attaches to oxygen while the electron moves to chromium...*", i.e., hydrogen transfer occurs in such a manner that the electron moves to chromium while the proton attaches to oxygen and the reaction $Cr^{VI}O_2Cl_2 + H{-}R \rightarrow HOCr^V(O)Cl_2 + R^\bullet$ "*...could be termed proton-coupled electron transfer*".[635] The role of an ET component in the H-abstraction with CrO_2Cl_2 may be represented by a structure where the hydrocarbon part has a substantial radical−cation character (Scheme 16).

Scheme 16. Polarization of the TSs for the Hydrogen Abstraction with CrO_2Cl_2



Scheme 17. Oxidative Addition of CrO_2Cl_2 to the σ_{C-C} Bond



The oxidation of the σ_{C-C} bonds[640] of propellanes with CrO_2Y_2 (Y = Cl, OAc) revealed the involvement of radical cations: the reactions mainly resulted in *dinucleophilic* Y^- addition (Scheme 17). Radical cation **A** formed in the first step is trapped giving radical **B** or **D**. Further reactions of **D** with CrO_2Y_2 either via abstraction of Y or through O addition gave dinucleophilic addition product **E**. Radical **B** rearranges to a stable ketone complex with the reduced chromium reagent (Ètard complex **C**). The formation of radical cations through oxidations of non-hydrocarbon substrates with Cr^{VI} reagents is well-documented.[641]

Computational VB,[632] ab initio, and DFT studies[642,643] on a series of M=O species involving d^0 metals also indicate that the C−H bond activation takes place via a hydrogen-abstraction channel rather than through concerted M=O [2 + 2]-addition to the C−H bond.

A very similar mechanistic behavior was proposed for the reactions of the permanganate anion MnO_4^- with alkanes. Recently,[644] the transition structure for H-abstraction from methane was analyzed at the B3LYP/6-311+G(d,p) level (the barrier is 32.3 kcal mol^{-1}). The TS is later than the one for the reaction of CH_4 with oxygen-centered radicals, and it was concluded that "*The permanganate mechanism fits the oxygen rebound mechanism*". The rebound mechanism takes place for the reactions with different Mn=O species, and the H-abstraction scheme is in agreement with early mechanistic proposals[642,645] (3°:2°:1° = 2100:60:1 for the alkane oxidations with the $KMnO_4/CF_3COOH$ system) and with more recent kinetic studies of the oxidations with n-Bu_4NMnO_4.[646] Probably the same mechanistic scenario is valid for the RuO_4 oxidations of hydrocarbons (despite early interpretations suggesting concerted insertion based on the absence of rearranged products and the stereoselectivity of the substitution).[647,648]

The selectivities observed in the oxidations of adamantane with oxo−ruthenium species[649] (3°:2° = 93) and potassium ferrate[650] (>30) are exceptionally high and involve a $M^{VI}{=}O + R{-}H \rightarrow M^V{-}OH + R^\bullet$ activation step and a "*highly polar transition state*"[651] (Scheme 16). The same mechanism probably is valid for the oxidations of *cis*-decaline,[651] *endo*-tetrahydrodicyclopentadiene,[652] and cyclohexane.[653] However, in the latter case no radical trapping chlorination products were found in the presence of CCl_4. The adamantane bridgehead-substituted products were the only ones reported for oxidation with bis(tosylimido)ruthenium(VI) porphyrins[654] and for the amidation with PhI═NTs catalyzed by ruthenium non-porphyrin complexes.[655] The adamantane amidation with PhI═NTs in the presence of the dirhodium catalyst show 3°:2° = 44.[656] Correlation of 1-substituted adamantanes + RuO_4 reaction rates with the Taft σ^* constants gave $\rho^* = -2.08$, indicating a polar TS.[657] The observed selectivities with the M═O reagents could be attributed to ET contributions in the TS which lead to preferential formation of the C_{3v} adamantane radical cation with a half broken 1-Ad−H bond (vide infra). The participation of oxo−ruthenium species was proposed for the $RuCl_3$-catalyzed oxidation of alkanes with CF_3COOOH[658] or CH_3COOOH/CF_3COOH[659] and for Ru^{III} complexes with tris(2-pyridylmethyl)amine in the presence of *m*-CPBA.[660,661] However, the selectivities of adamantane oxidations (3°:2° = 25−30) seem too low to draw such mechanistic conclusions.

3.3. In Situ Generated Metal−Oxo Species

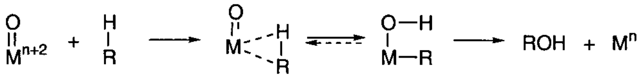
3.3.1. Cytochrome P450

It is highly probable that the cytochrome P450-catalyzed[38,662] hydrocarbon oxidations, which give hydroxy derivatives, involve a C−H activation step with an Fe═O group bound to the porphyrin moiety;[8,663] some analogies to other metal−oxo reagents (like CrO_2Cl_2, or non-heme M═O species) were drawn recently.[664−670] Formation of an active Fe═O state requires several steps through the Fe−OOH species[663,671,672] (deprotonation leads to the loss of alkane hydroxylation activity[673]).

Initially, concerted C−H insertion mechanisms were proposed based on essentially complete stereoselectivities.[674] A number of radical clock[675] experiments with methylcyclopropanes,[676] methylcubanes,[408] and bicyclo[2.1.0]pentane showed that the intermediate radical pair collapses at a rate $>10^9$ s^{-1},[677] and the homolytic rebound pathway initially proposed[678−680] became generally accepted[681] (see, however, ref 682). In addition, comparable KIEs for the P450,[683,684] M═O,[685−687] and *t*-BuO$^\bullet$ hydroxylations of the same set of substrates lent strong evidence for "...*a common hydrogen atom transfer mechanism*".[688] Nevertheless, correlations between the ratio of rearranged to unrearranged products in the reactions of hydrocarbons with P450 and with independently generated radicals are poor. As a consequence, a cationic channel for the oxidation with P450 was proposed.[689,690] Radical clock experiments with hypersensitive alkylcyclopropanes do not support the alternative σ-complex ("agostic complex" model, Scheme 18)[691] but show that the "*oxygen rebound mechanism ...is not complete*", implicating a cationic mechanism.[692]

A reconciliation of the contradicting experimental data was offered[614,693−695] invoking a two-state[115,116] concerted insertion/rebound mechanism. The key mechanistic point drives at the fact that the Fe═O reagent is stable in the energetically close-lying doublet and quartet spin states. The C−H bond activation involves hydrogen-atom abstraction[392,696] (Scheme 19) both on the high (quartet $^4\mathbf{TS_{abs}}$) and the low-spin state (doublet $^2\mathbf{TS_{abs}}$) surfaces (the barriers[392,696] are virtually the same, ca. 26 kcal mol^{-1} at B3LYP/LACVP-6-31G). The resulting high-spin state ^{4}**MIN2** has a *substantial barrier* for the rebound path via $^4\mathbf{TS_{reb}}$ (5.5 kcal mol^{-1}), while the recombination from low-spin ^{2}**MIN2** is *barrierless*.[392,696] Notably, the carbon atom of **MIN2** formed after the H-abstraction step has radical character (the spin density is 0.96 on R = CH_3). Owing to a substantial barrier for recombination through $^4\mathbf{TS_{reb}}$, this radical can rearrange on the high-spin potential energy surface. Similar transition structures were later found[697] at the B3LYP/D95-DZ-TZV level for the H-abstraction from ethane by another model Fe−porphyrin (the computed H-abstraction barriers on the quartet and doublet surfaces were 28.4 and 22.2 kcal mol^{-1}, respectively), but the barriers for the rebound were not recognized. Further MD studies for the reaction (−S−Cys = $-SCH_3$, Scheme 19)[698] and ethane (RH = C_2H_6 and −S−Cys = $-SCH_3$, Scheme 19) at the DFT level show strong participation of porphyrin moiety in the energy transfer during oxidation process.[667,699] The calculated KIEs for model P450 transition structures agree nicely with those determined for H-abstraction reactions with the oxygen-centered *t*-BuO radical[392] and actual P450.

Scheme 18. "Agostic" Mechanistic Model for the C−H Activation with Metal−Oxo Reagents

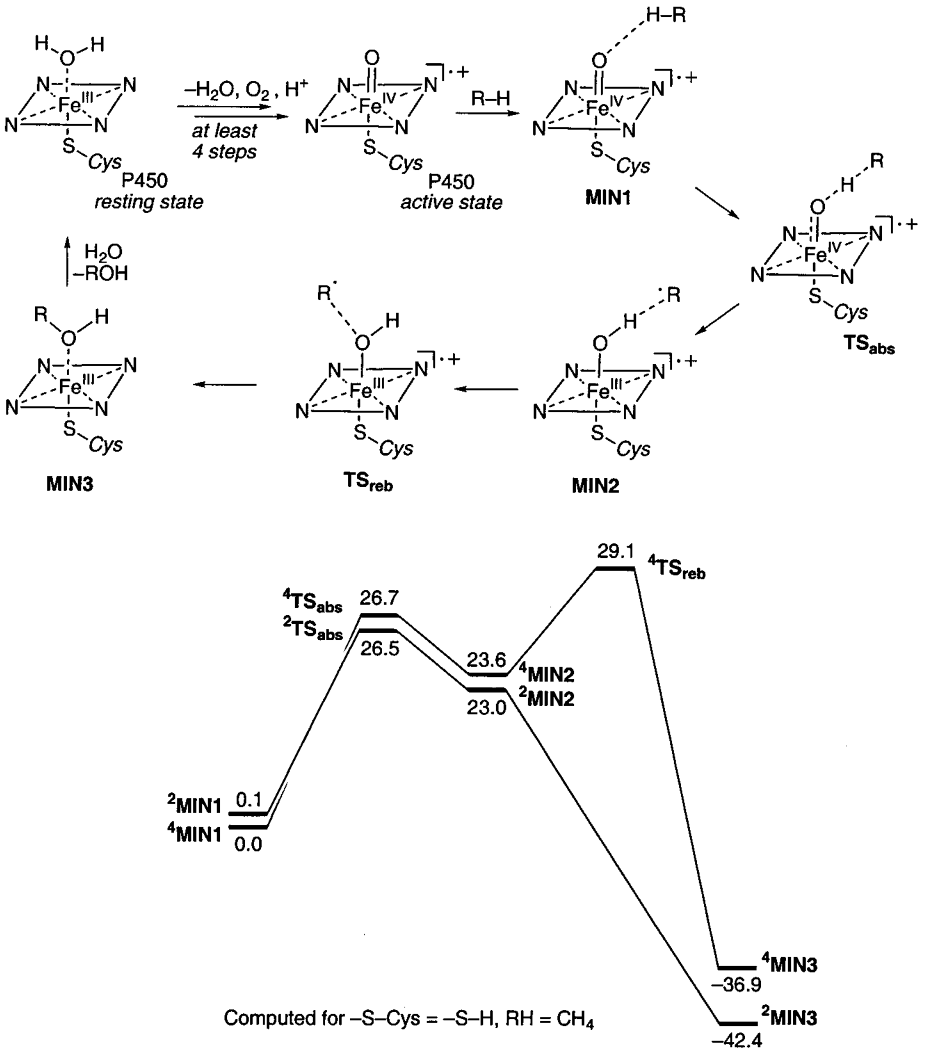


The two-state model for P450 action[614,700] was recently challenged by experimentalists [670,682,690,701,702] as it was shown that Fe−OOH[703] (or Fe−OOR for model porphyrins[701]) itself is able to activate alkanes and "*two competent hydroxylating species*,"[703] i.e., both Fe−OOH and Fe═O may be involved in the reactions of P450 with the C−H bond.[670]

An important observation is that the polar character of the TSs for the H-abstractions with the P450 models may be "...*manifested as a formal one-electron oxidation of the alkane*"[696] as the net positive charge on the hydrocarbon part of the TS is about +0.3e even for such a poor donor as methane. It is worth mentioning that the radical cationic pathway is consistent with earlier observations on quadricyclane oxidations with P450.[704] The ability of P450 to oxidize aromatics with formation of radical cations[705] was demonstrated independently and debated for some other substrates such as amines.[706] This is consistent with the high oxidative properties of P450 (the $E_{1/2}$ value was estimated[707] as 1.85 V vs SCE).

The above mechanistic suggestions may be extended to the alkane biotransformations with several fungal systems[41,42] and a number of P450 isoforms,[708,709] which demonstrate alkane hydroxylation abilities involving Fe═O species.

Scheme 19. Multistate Reactivity Model for Methane Activation with P450 (ΔE, kcal mol^{-1}, B3LYP/LACVP-6-31G)

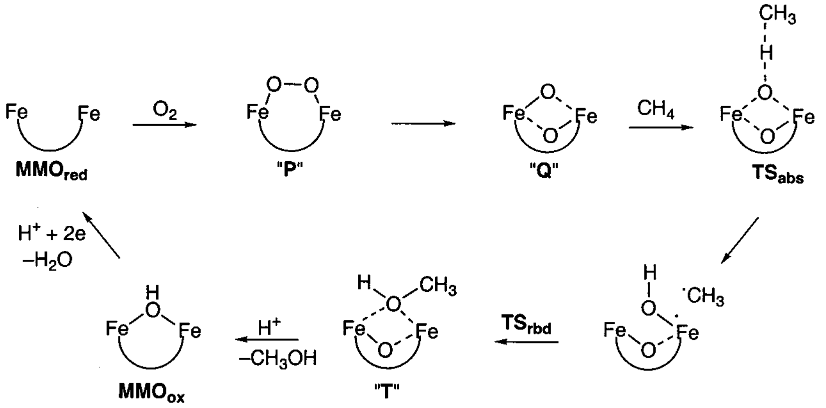


3.3.2. Methane Monooxygenase

Methane monooxygenase (MMO), the *"P450 in a wolf's clothing"*,[710] is able to catalyze the oxidation of hydrocarbons, which are inert toward P450. One of the most intriguing aspects of methane chemistry is the selective oxidation to methanol catalyzed by soluble MMO.[386] MMO is a homogeneous enzyme which contains[711−713] a diiron non-heme reactive center,[714] a ribonucleotide reductase, as well as another protein, the so-called component **B**,[715] which couples them.[716] Despite quite a number of attempts to model MMO-like systems[717−726] by studying the catalytic activity of different diiron complexes with methane[727−732] and higher alkanes,[733−738] the mechanisms for the activation and reduction steps and the role of carbon-centered radicals are not entirely clear.[39,40,739,740] The importance of radicals in enzymatic alkane cleavages of C−H bonds was pointed out in 1990.[741] It was suggested that *"...direct OH abstraction by $CH_3^{\bullet}$ cannot be excluded..."*.[742] The complex mechanism (Scheme 20) for methane oxidation with MMO was thoroughly studied[742] and involves oxygenation of the MMO to "**P**", followed by rearrangement to active "**Q**" (or diiron-oxo form "**R**", not shown), which is able to abstract hydrogens from hydrocarbons ($\mathbf{TS_{abs}}$). Formation of the radical pair is followed by the rebound to "**T**" via $\mathbf{TS_{rbd}}$ and the elimination of methanol to form $\mathbf{MMO_{ox}}$. The reduction of $\mathbf{MMO_{ox}}$ recovers the starting resting state of the enzyme ($\mathbf{MMO_{red}}$) and completes the cycle.

The MMO reactions were modeled computationally at the B3LYP/SBK level for methane reacting with a diiron model complex $(NH_2)(H_2O)Fe(\mu\text{-}O)_2(\eta^2\text{-}HCOO)_2Fe(NH_2)H_2O$.[103,743] The transition structure for the H-abstraction ($\mathbf{TS_{abs}}$, Scheme 20, the barrier is 19 kcal mol^{-1}) was located; abstraction is followed by a low-barrier migration and rebound of the H_3C radical via a 6 kcal mol^{-1} barrier ($\mathbf{TS_{rbd}}$). The final state "**T**", a weakly bound Fe···methanol complex, is ca. 30 kcal mol^{-1} more stable than the initial cluster with methane, making the overall reaction highly exothermic. Some other B3LYP computations were performed for diiron model complexes containing histidine and glutamic acid moieties.[744,745] The barrier for H-abstraction from methane for a much more realistic model intermediate **"Q"** at the B3LYP/LACV3P-6-31G(*d*) level is about 13 kcal mol^{-1}.[730] It was found, however, that the *oxygen activation* of the dimer iron complex (modeling the "**P**" → "**Q**" reaction, Scheme 20) has the highest barrier (17 kcal mol^{-1});[744]

Scheme 20. Schematic Representation of the Key Intermediates of Methane Activation with MMO



the barrier for the H-abstraction from methane modeling TS_{abs} was computed to be lower and in the range of 10−13 kcal mol^{-1}.

Kinetic experiments demonstrate that methane oxidation is even more complex and that at the stage of "**Q**" there may be "*two methane molecules* [...] *involved in the decay process*".[746] The specificity of MMO for methane oxidations was pointed out based on a two-step "**Q**" decay process: The E_a values (26−30 kcal mol^{-1}) for the formation the reactive intermediate "**Q**" are independent of the alkane structure. Generally, methane is oxidized faster than other substrates with weaker C−H bonds and "*only small normal alkanes are hydroxylated*" with "particulare" MMO due "*to a short and narrow hydrophobic pocket*".[747]

The relatively high barriers for the rebound step show that the lifetimes of weakly bound hydrocarbon radicals formed after the H-abstraction step may be high enough to allow for side reactions, e.g., enantiomerizations or/and rearrangements. This depends first of all on the structure of the radical: Chiral CH_3-CHDT is oxidized by MMO with partial inversion of configuration;[748] however, *all*-*exo*-d_4-norbornane epimerizes.[749] The prochiral CH_2 groups of *n*-butane and *n*-pentane were hydroxylated with 46% and 80% *ee*, respectively.[750] Methylcyclopropane radical clocks[751,752] gave at most small amounts of rearranged products, showing that the rebound reaction is fast.[675,753] Attempts to use ultrafast radical clocks based on methyl cubanes gave unrearranged cubylmethanol with MMO from *methylococcus capsulatus*[408] and a number of unrearranged as well as rearranged products with *methylosinus trichosporium* OB3b.[754] A reinvestigation of the methylcubane oxidation with MMO, however,[755] demonstrated that the rearranged product was homocuban-1-ol which cannot form through a radical pathway from methylcubane. It was concluded that "*no radical intermediates are formed*". Already at the beginning of the 1990s it was stated that "*a significant component of the hydroxylation reaction pathway does not proceed through a radical intermediate*";[753] at the same time, high KIEs (about 5) showed that C−H bond breaking is rate limiting. The KIEs for methane oxidation with MMO based on product analysis[77,756] vary from a maximum value of 19 for the CH_4/CD_4 couple to 4 for CH_4/CH_3D, i.e., these are quite normal for the reactions of methane with radical species. The latter value is close to that found for CH_3CHDT (KIE = 4.2 ± 0.2).[748] At the same time the decay of intermediate "**Q**" displays abnormally high KIEs (50−100 for the CH_4/CD_4 couple),[77,756] presumably due to tunneling contributions[67] or anomalously high secondary[78] isotope effects.

The radical rebound mechanism is probably operative for other diiron monooxygenases like, for instance, from *pseudomonas oleovorans* (AlkB) which can grow on octane as a carbon source. Recent radical clock experiments on norcarane hydroxylations enabled the detection of a radical pathway, and in analogy to the two-state situations in P450 chemistry, it was concluded that the "*...possible spin state crossing effects are in need of careful scrutiny*".[757]

4. Oxidative Alkane Activations and Hydrocarbon σ-Radical Cations

$$\mathbf{R{-}H - e^- \rightarrow R{-}H^{\bullet +}}$$

Alkane oxidation by removal of an electron through an outer-sphere ET[758,759] gives a radical cation paired with the reduced oxidant.[760,761] This is typical for the oxidation of hydrocarbons with neutral photoexcited species (predominantly substituted aromatics)[72,762,763] but is not very effective with respect to the overall energy consumption (back ET dominates).[764] For sterically unhindered donors under photooxidations[759,765] or with charged oxidants an inner-sphere SET[137,758] is possible. Irradiation of alkanes in matrixes is another way to hydrocarbon radical cations, which may be directly observed at low temperatures.[766−769]

SET alkane activations often are more selective than electrophilic radical activations because one electron is removed from a HOMO with σ-character, and the ionized species thus obtained are denoted as σ-radical cations which possess a definitive structure in many cases.[770] As the electron is removed from a bonding orbital, the σ-radical cations have one or several partially broken (elongated) σ-bonds.[771] If the HOMO of the hydrocarbon is degenerate, the resulting radical cation distorts in accordance with the Jahn−Teller theorem.[772,773] Radical cations can undergo proton or hydrogen-atom loss[774−776] (vide supra) with formation alkyl radicals or carbocations undergoing rearrangements[777,778] or C−C bond fragmentations.[770,779−781] The selectivities of these transforma-

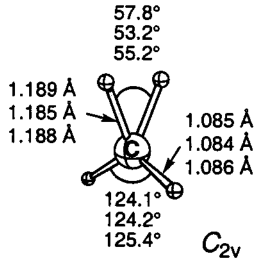


Figure 11. Structure of the methane radical cation at B3LYP (first entry), MP2 (second entry), and QCISD (third entry) levels with a 6-311G(*d*,*p*) basis set.[811]

tions are closely related to the structures of the incipient radical cation as analyzed below.

Attention will also be paid to recent computational data on the structure and transformations of hydrocarbon σ-radical cations which still represent a formidable computational challenge.[782−792]

4.1. Acyclic Alkanes

4.1.1. Methane

The simplest alkane radical cation derives from T_d-methane which distorts to lower symmetry upon ionization of one of the triply degenerate HOMOs.[793] Early ab initio computations revealed two stable structures with D_{2d} and C_{3v} symmetries;[794−796] however, based on vibrational analysis, first in 1973 at CI[797] and later at higher levels,[798−804] the lowest-energy C_{2v}-symmetrical minimum for $CH_4^{\bullet+}$ (Figure 11) was found. However, the C_{2v} structure is a TS at several DFT levels where the D_{2d} structure is a minimum.

The barrier for the interconversion of the degenerate C_{2v} structures via a C_s-symmetrical TS is very low (1.1 kcal/mol^{-1} including ZPVE corrections at MP4/6-31G(*d*,*p*)//MP2/6-31G(*d*,*p*),[802] making the $CH_4^{\bullet+}$ structure highly fluxional. The ESR spectrum of $CH_4^{\bullet+}$ in a neon matrix at 4 K consists of a quintet resulting from equalization of all hydrogens[805] due to the fluxional behavior of $CH_4^{\bullet+}$ or tunneling.[806,807] The ESR[807] and high-resolution zero-kinetic-energy PE[808] spectra of $CD_2H_2^{\bullet+}$ clearly support a C_{2v} ground state of $CH_4^{\bullet+}$. The neon matrix may affect the hyperfine coupling constants,[809] because the interactions of $CH_4^{\bullet+}$ with noble-gas atoms is not negligible (2 kcal mol^{-1}).[810] Temperature, vibrational, and matrix effects on the geometry and hyperfine constants for the methane radical cation were analyzed at B3LYP/6-311G(*d*,*p*) and by utilizing DFT molecular dynamics simulations.[811] Note, however, that the arrangement with the experimental data is poor. The experimental ionization potentials for methane[812] are high ($I_v = 13.6$ eV,[813] $I_a = 12.6$ eV).[814] The most favorable *intramolecular* gas-phase reaction of $CH_4^{\bullet+}$[815] is the formation of the methyl cation CH_3^+: the ion dissociation threshold is 14.3 eV, and the BDE for the $(H{-}CH_3)^{\bullet+}$ is 1.7 eV.[816] Formation of the methyl radical through the *intermolecular* $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^+ + CH_3^{\bullet}$ collision reaction is −0.2 eV exothermic.[817]

Methane activation with strong electrophiles is one of the major achievements of superacid chemistry.[18,165] The original mechanistic rationalization is based on the direct attack of the electrophile on the C−H bonds.[14,163,818,819] Such a mechanistic scenario, however, is difficult to verify computationally or to support experimentally, because the highly exothermic protonation of alkanes occurs without an activation barrier; only product distributions rather than transition structures can be analyzed.[167,820−832] The mechanisms for the methane activation with electrophiles which are more stable than the proton, were studied over the past decade for a number of reagents, e.g., carbocations,[833] NO^+,[834,835] $H_3O_2^+$,[836,837] $SO^{\bullet+}$,[838] "F^+",[839] B,[840] B_2,[841] BH_2,[842] Cl_3^+,[843] Cl_2H^+,[844] electrophilic Pt complexes,[845−847] $M{=}O^{n+}$ species,[848−851] and bare metal ions.[849,852−855] The computational results show that the electrophilic attack is directed toward the *atoms* (C or H) rather than the C−H or C−C bonds; this is exemplified by the TS for the CH_4 activation with NO^+[834] and $Fe{=}O^{2+}$ (Figure 12).[850] In this context, the very similar geometric features of the methane radical cation (Figure 11) and the hydrocarbon moieties of the transition structures for methane activation with NO^+ and FeO^+ should be emphasized: the TSs resemble inner-sphere electron-transfer structures. That is, electrophilic alkane activation is an extreme case for the ET oxidation of alkanes, where recombination and electron-transfer occur in one step (vide infra).

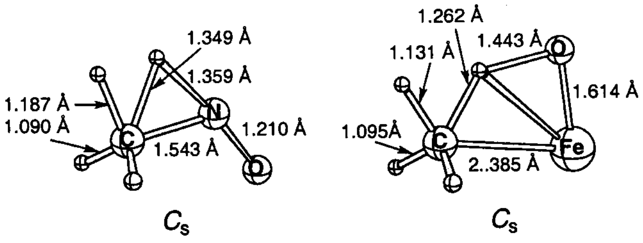


Figure 12. TSs for the attack of NO^+ (MP2/6-31G(*d*)[834] and $Fe{=}O_2^+$ (B3LYP/6-311G(*d*,*p*))[850] on the carbon atom of methane.

The computations clearly show that the mechanistic features for methane activation with charged electrophiles are characterized by direct carbon attack through a strongly polarized transition structure. The net charge on the hydrocarbon part of the TS with NO^+ is about +1e, and the structure of the CH_4 fragment is only slightly distorted from the structure of free $CH_4^{\bullet+}$ (Figures 11 and 12). Thus, the most realistic representation of the activation process is inner-sphere electron transfer from methane to the electrophile which formally results in the C−H insertion. A number of data on the formation of *free* $CH_4^{\bullet+}$ (outer-sphere SET)[508,856] in acidic media in the presence of metal ions[857] probably follow a similar reactivity pattern, and detailed mechanistic studies show "*that outer-sphere electron transfer or bond homolysis...did not occur*".[858]

4.1.2 Ethane

The ethane radical cation is another interesting Jahn−Teller system. The C_{2h}-symmetrical doubly degenerate HOMO of ethane describes mainly the C−H bonding and is very close in energy to the D_{3d}-symmetric HOMO-1 which resembles the C−C bond. Early computations[796] show a preference of the radi-

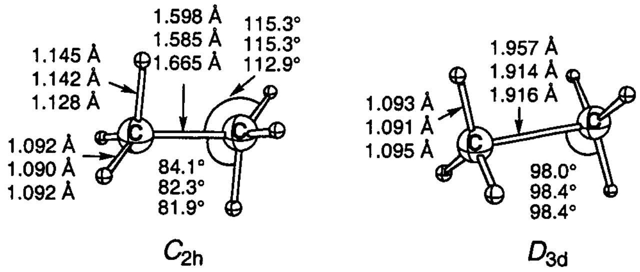


Figure 13. Two structures of the ethane radical cation at B3LYP (first entry), MP2 (second entry), and CCSD(T) (third entry) levels with a DZP basis set.[782]

cal cation for a D_{3d}-symmetrical structure ($^2A_{1g}$ state) with a long C−C bond; however, the "diborane-like" C_{2h} structure (^2A_g state) with elongated C−H bonds also is a true minimum.[801,859−863] Both structures (Figure 13) are very close in energy,[864] but C_{2h}-$C_2H_6^{\bullet+}$ is 1.3 kcal mol^{-1} more stable at DFT with a large basis set (B3LYP/6-311++G(3*df*,3*pd*)//B3LYP/6-311G-(*d*,*p*)), 0.4 kcal mol^{-1} at QCISD(T)/6-311G(*d*,*p*),[865] and 0.3 kcal mol^{-1} at CCSD(T)/TZ(2*df*,2*pd*)//CCSD(T)/TZ2P.[782] It was concluded that "*...only one thermally averaged C_{2h} structure should be observed*".[782] This is consistent with the experimental (at 4.2 K)[866] and computed[859,861] ESR spectra of $C_2H_6^{\bullet+}$. The experimental vertical ionization potential of ethane (the recommended value is 11.52 eV[867]) which exhibits strong nonadiabatic behavior upon ionization[868] is hard to reproduce computationally.[865,869]

The most fundamental reaction of $C_2H_6^{\bullet+}$ is dihydrogen elimination leading to the relatively stable ethylene radical cation: $C_2H_6^{\bullet+} \rightarrow C_2H_4^{\bullet+} + H_2$. The reaction is +7.8 kcal mol^{-1} endothermic at QCISD(T)/6-311++G(2*gf*,2*pd*), and the computed[870] barrier is 15.6 kcal mol^{-1} without inclusion of tunneling contributions. This is 1.5−2.4 kcal mol^{-1} larger than the experimental value[871,872] obtained from the photoion coincidence (PEPICO) spectrometry;[873] tunneling[874,875] probably contributes substantially to this reaction.

As noted for the reactions of methane with weak electrophiles but strong oxidizers (e.g., NO^+), the activation of ethane with such species also involves TSs or intermediates reminiscent of the ethane radical cation.[876−879] Again, the oxidation of ethane with many electrophiles occurs as an inner-sphere SET and does not involve the free ethane radical cation.[508,880]

Another well-studied reaction of $C_2H_6^{\bullet+}$ is the interaction with nucleophiles: The theory of the nucleophilic additions to radical cations[881,882] was developed using ab initio computations and curve-crossing models.[136,137,883] The reactivity of $C_2H_6^{\bullet+}$ with the model nucleophile H_2S was studied at the HF[884] and, with number of nucleophiles, MP2//QCISD-(T)[137,885] levels of theory. The backside approach of water as the nucleophile via a transition structure **B** (Figure 14) is almost barrierless in the gas phase; the frontside approach via **F** is highly unfavorable (the barrier is 23.3 kcal mol^{-1}).

The preference for the backside approach was shown for a number of other nucleophiles (H_2S, NH_3, PH_3, HF). The SCRF solvation model applied to the

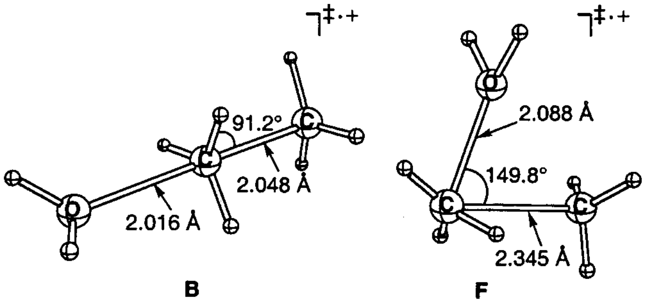


Figure 14. Transition structures for the backside (**B**) and frontside (**F**) attack of a model nucleophile (H_2O) on the ethane radical cation at MP2/6-31G(*d*).[885]

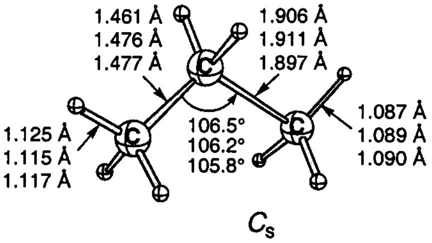


Figure 15. Structure of the propane radical cation at B3LYP (first line), MP2 (the second line), and QCISD (third line) levels with a 6-311G(*d*,*p*) basis set.[865]

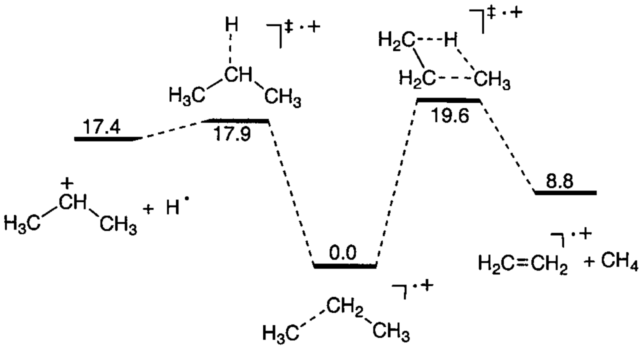
TSs in the $H_2S/C_2H_6^{\bullet+}$ system shows an increase of the barriers for backside addition in polar solvents from 0.5 kcal mol^{-1} in the gas phase to 6.2 kcal mol^{-1} in acetonitrile; the solvent effect on the barriers for frontside addition is small.

4.1.3. Propane

Propane, the next member of this family, has a nondegenerate C_{2v} ground state and, thus, is Jahn−Teller inactive. As a consequence, the radical cation $C_3H_8^{\bullet+}$ could maintain the symmetry of the parent neutral hydrocarbon. However, the C_{2v} structure with two elongated C−C bonds being a minimum at MP2/6-31G(*d*)[801,886,887] is a transition state at B3LYP with the 6-31G(*d*), 6-311G(*d*,*p*), and 6-311G(2*d*,*p*) basis sets as well as at QCISD(T)/6-311G(*d*,*p*).[865] The C_s structure with one long C−C bond (Figure 15) is the global minimum for this part of the PES and agrees well with ESR data for $C_3H_8^{\bullet+}$ at 4 K;[888] however, the difference between the C_{2v} and C_s structures is less than 1 kcal mol^{-1} at QCISD.[887] The "one long C−C" bond structures are typical for open-chain alkane radical cations (vide infra). The B3LYP-computed vertical ionization potential 11.54 eV[889] of propane is in excellent agreement with experiment.[865]

The fragmentation pathways of the propane radical cation were investigated experimentally and theoretically. Identified were the elimination of methane[890] $C_3H_8^{\bullet+} \rightarrow C_2H_4^{\bullet+} + CH_4$ ($k = 3.2 \times 10^4$ s^{-1} or 1.1×10^4 s^{-1}) or of a hydrogen atom[891] $C_3H_8^{\bullet+} \rightarrow C_3H_7^{+} + H^{\bullet}$ ($k = 6.3 \times 10^5$ s^{-1}). Both pathways were studied computationally at QCISD(T)/6-311+G(2*d*,2*p*)//MP2/6-31G(*d*).[887,892] Hydrogen loss from the CH_2 moiety ($\Delta H^{\ddagger} = 17.9$ kcal mol^{-1}) leads to the *sec*-propyl cation and is more favorable than $H^{\bullet}$ loss from the CH_3 group ($\Delta H^{\ddagger} = 28.2$ kcal mol^{-1}) forming corner-protonated cyclopropane. The fragmentation to $C_2H_4^{\bullet+} + CH_4$ occurs via a loosely bound ion−neutral TS and

Scheme 21. Transformations of the Propane Radical Cation Computed at the QCISD(T)/6-311+G(*2d,2p*)//MP2/6-31G(*d*) Level (kcal mol^{-1})



is thermodynamically favored (Scheme 21). The experimental rate constants for these reactions are reproduced reasonably well by RRKM calculations.[892]

4.1.4. Butanes

A number of computational[893,894] and experimental ESR data are available for radical cations derived from *n*-butane[800,801,866,893,894] and isobutane.[800,866,894] The structural changes in the radical cations vs the neutrals are substantial, and the differences between the experimental vertical I_p (11.0−11.2 eV) and adiabatic I_a (10.3−10.6 eV) are large.[889] The most stable structure for $n\text{-}C_4H_{10}^{\bullet+}$ is C_{2h}-symmetric with a long central C^2-C^3 bond (Figure 16); $i\text{-}C_4H_{10}^{\bullet+}$ also forms a long C−C bond minimum (C_s symmetry).

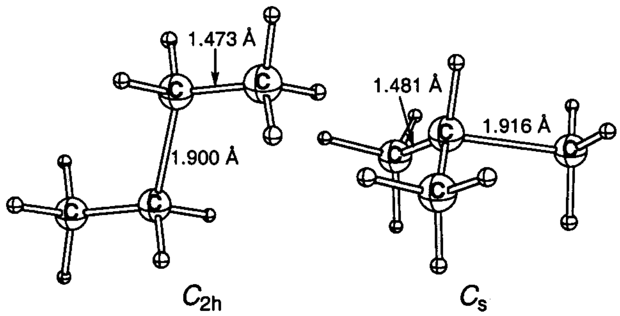


Figure 16. Structures of the *n*-butane and isobutane radical cations at MP2/6-31G(*d*).[894]

$n\text{-}C_4H_{10}^{\bullet+}$ rearranges to $i\text{-}C_4H_{10}^{\bullet+}$ through a 19.4 kcal mol^{-1} barrier. The most favorable and experimentally observed[895,896] follow-up reaction (Scheme 22) is the $i\text{-}C_4H_{10}^{\bullet+} \rightarrow H_3CCH{=}CH_2^{\bullet+} + CH_4$ fragmentation which is −0.4 kcal mol^{-1} exothermic at the QCISD(T)/6-31G(*d,p*)//MP2−6-31G(*d*) + ΔZPVE level (the experimental reaction enthalpy is −1.3 kcal mol^{-1}).[894] The complex $(H_3CHC{=}CH_2{\cdots}CH_4)^{\bullet+}$ forms −2.7 kcal mol^{-1} exothermically.

4.1.5. Higher Acyclic Alkanes

The fragmentation pathways for the radical cations derived from pentanes[866,897−899] are very complex and preferentially lead to loss of CH_4 or C_2H_4 in the gas phase. The gas-phase behavior of alkane radical cations is clearly different from that in matrixes[900] where the initial reaction involves proton transfer to a neutral partner hydrocarbon C_mH_{2m+2} (eq 26), i.e., hydrocarbon radical cations behave like strong acids. The protonation can be accompanied by a number of secondary reactions, for instance, dihydrogen loss (eq 27), which is typical for the superacidic[13,164,165] behavior of protonated alkanes.

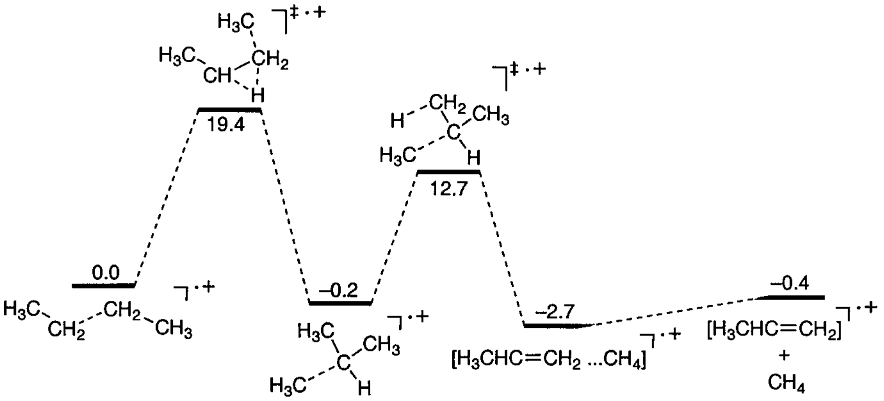
$$C_nH_{2n+2}^{\bullet+} + C_mH_{2m+2} \rightarrow C_nH_{2n+1}^{\bullet} + C_mH_{2m+3}^{+} \tag{26}$$

$$C_mH_{2m+3}^{+} + Nu^{-} \rightarrow C_mH_{2m+1}Nu + H_2 \tag{27}$$

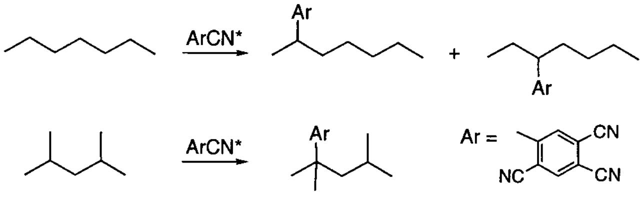
A number of studies on the reactivities of $C_nH_{2n+2}^{\bullet+}$ in the condensed state were performed for pentane,[901] 2-methylpentane,[902] hexane,[903] heptane,[904−907] octane,[906,908] decane,[909] and undecane.[910] Some of the radical cation reactions demonstrate high selectivities for deprotonation, which occurs from the primary position[903] and which leads to the functionalization of the penultimate position of the parent neutral hydrocarbon (eqs 26 and 27). This was demonstrated by the selective oxidation of *n*-octane to 2-chlorooctane with the heptane radical cation in CCl_3F matrixes at 77 K (eq 26, $n = 7$, $m = 8$; eq 27, $m = 8$, Nu = Cl).[905]

Proton transfer from alkane radical cations is a process which dominates also in solution. Oxidation of a number of linear and branched alkanes with photoexcited 1,2,4,5-tetracyanobenzene (TCB) was introduced as a preparative method for alkane functionalization.[763] In contrast to the reactions in solid matrixes, deprotonation occurs mainly from the 2°

Scheme 22. Transformations of the *n*-butane Radical Cation Computed at the QCISD(T)/6-31G(*d,p*)//MP2/6-31G(*d*) Level (kcal mol^{-1})



Scheme 23. Oxidation of Linear and Branched Alkanes with Photoexcited TCB



(*n*-hexane) and 3° (2,5-dimethylpentane) positions of the alkane (Scheme 23).

Another reaction of branched hydrocarbon radical cations also is the loss of H_2. These reactions were studied experimentally[911] and computationally[912] for the 2,3-dimethylbutane radical cation (eq 28), and significant tunneling was indicated.

$$(CH_3)_2CH{-}CH(CH_3)_2^{\bullet+} \rightarrow (CH_3)_2C{=}C(CH_3)_2^{\bullet+} + H_2 \quad (28)$$

4.2. Cyclic Alkanes

4.2.1. Cyclopropane

Quite a number of contributions describe the computational[800,913−919] as well as experimental[920] studies on the cyclopropane radical cation. The HOMO of D_{2h}-symmetric cyclopropane is doubly degenerate (Figure 17), and ionization leads to a C_{2v}-symmetrical $^2A_1$ structure with one long C−C bond; the $^2B_2$ state with two long C−C bonds is a TS. The ESR spectrum of *c*-$C_3H_6^{\bullet+}$ strongly supports the $^2A_1$ C_{2v} structure.[921] This is in marked contrast to the phenylcyclopropane radical cation where the structure with two long C−C bonds is a minimum due to benzylic stabilization of both the radical and the cation site.[922,923]

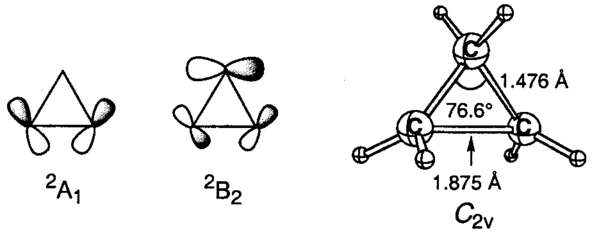
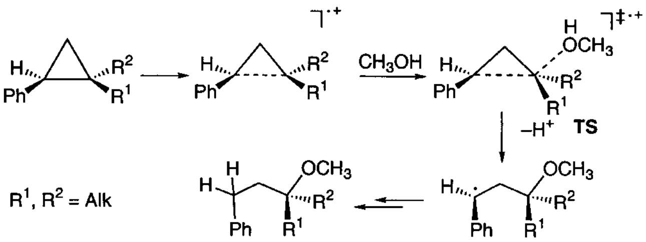


Figure 17. HOMOs of cyclopropane[915] and the stable form of the cyclopropane radical cation MP2/6-31G(*d*).[918]

The ring-opened form of *c*-$C_3H_6^{\bullet+}$, the "trimethylene radical cation",[924] is, despite a number of claims about its formation,[925,926] not a minimum[913] but rather the TS ($\Delta H^{\ddagger}$ = 30 kcal mol^{-1}) en route to the propene radical cation, which is 8.2 kcal mol^{-1} more stable than *c*-$C_3H_6^{\bullet+}$ (MP2/6-31G(*d*)).[918] In contrast, nucleophilic backside attack on the terminal carbon atom of *c*-$C_3H_6^{\bullet+}$, which was predicted theoretically,[927] is almost barrierless[885] and in agreement with the experimentally observed inversion of configuration for the ring opening of substituted cyclopropane radical cations (Scheme 24).[928,929]

The ring opening of substituted cyclopropanes via radical cation intermediates[926] was proposed for photochemical SET oxidations[929−935] and chemical oxidations with NO^+.[936]

Scheme 24. Ring Opening of Substituted Cyclopropane Radical Cations in the Presence of Nucleophiles



4.2.2. Cyclobutane

The experimental vertical ionization potentials for cyclobutane and cyclopropane are very similar (11.3 eV).[889] There are a number of stationary points (square, trapezium, kite, rectangle, rhombus) for the conformationally flexible cyclobutane radical cation at semiempirical and low ab initio levels.[800,937] Optimizations and vibrational frequency analyses at MP2/6-31G(*d*) show that only the D_{2h} rhombus is a minimum.[938] However, the DFT and QCISD methods show one imaginary frequency for the D_{2h} structure which is a transition state for interconversion of the two C_{2h} parallelograms (Figure 18).[939]

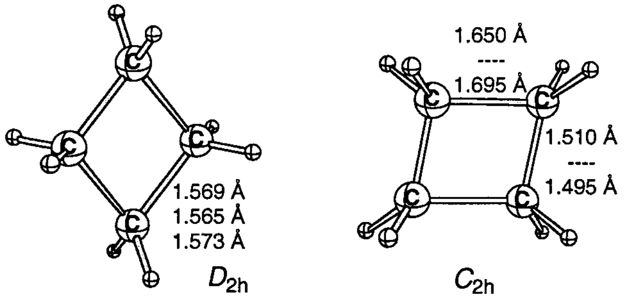


Figure 18. Structure of the rhombic (D_{2h}) and parallelogram (C_{2h}) structures of the cyclobutane radical cation at QCISD (first entry), MP2 (second entry), and B3LYP (third entry) with the 6-31G(*d*) basis set.[939]

The PES around this minimum is flat, and the distortion from planarity, which is observed experimentally in the 4.2 K ESR spectrum[940] of *c*-$C_4H_8^{\bullet+}$, was explained by packing forces in the frozen solvent.[938] The cycloreversion[941] of the cyclobutane radical cation to give the (ethene···ethene)$^{\bullet+}$ complex occurs concertedly via a 13.7 kcal mol^{-1} barrier.[939]

4.2.3. Medium-Sized Cycloalkanes

The experimental determination of the structures of radical cations generated from medium-sized cycloalkanes is hampered by their fast interconversion dynamics. A number of ESR experimental[916,942−944] and computational[916,919] studies were performed for the radical cations of cyclopentane and cyclohexane. *c*-$C_5H_{10}^{\bullet+}$ displays two energetically close structures with C_s and C_2 symmetries (Figure 19); the first is 1.9 kcal mol^{-1} more stable at B3LYP/6-311G(*d*,*p*); however, dynamic considerations, especially in the fast motion limit, favor the C_2 structure,[945] despite

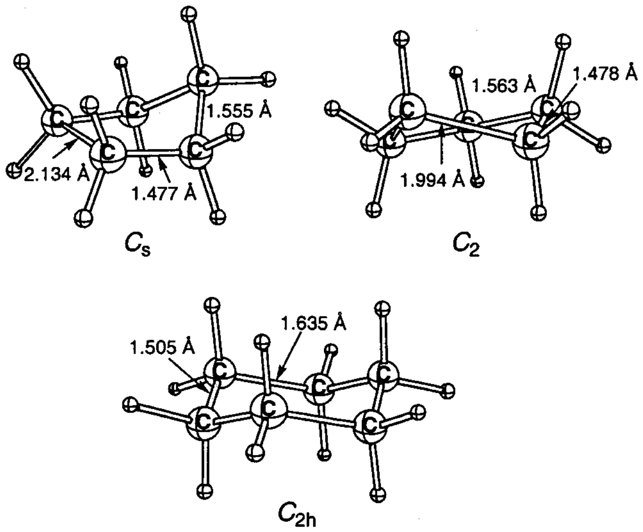
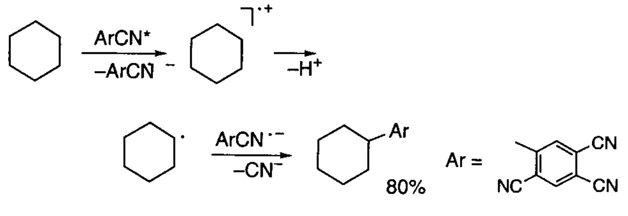


Figure 19. Structures of cyclopentane and cyclohexane radical cations at B3LYP/6-111G(*d*,*p*).[919]

Scheme 25. SET Oxidation of Cyclohexane with Photoexcited TCB



the latter being a transition structure both at MP2 and B3LYP levels (this work). The cyclohexane radical cation is C_{2h}-symmetric with two long C–C bonds;[946] the C_s starting structure converges to C_{2h} during the optimization[919] (Figure 19). Some computational and experimental data are available also for alkyl-substituted cyclohexane radical cations.[947–951]

Cycloalkane functionalization via radical cations was developed in solution.[952,953] For instance, cyclohexyl-benzene-1,2,4-tricarbonitrile was obtained in 80% yield after SET oxidation of cyclohexane with photoexcited TCB (Scheme 25).[763]

Electrochemical oxidation of cyclic alkanes in trifluoroacetic acid is accompanied by ring contraction of secondary to tertiary cations. These may form through a stepwise ECE process (eqs 29 and 30)[12] or, alternatively, through a two-electron oxidation[763] (eq 31). The deprotonation of the radical cation occurs in the solvent cage and is quite complex: The dynamics of hydrocarbon radical cations in solution was studied by Trifunac's group[954–957] and by others.[958]

$$\mathrm{R{-}H} - e^- \rightarrow \mathrm{R{-}H}^{\bullet+} \rightarrow \mathrm{R}^\bullet + \mathrm{H}^+ \qquad (29)$$

$$\mathrm{R}^\bullet - e^- \rightarrow \mathrm{R}^+ \qquad (30)$$

$$\mathrm{R{-}H} - 2e^- \rightarrow \mathrm{R}^+ + \mathrm{H}^+ \qquad (31)$$

4.3. Polycyclic Hydrocarbons

4.3.1. Bicyclobutane

The HOMO of *bicyclo[1.1.0]butane*,[242] the simplest bicyclic compound, mainly describes the central C–C bond between the tertiary carbon atoms, and ionization leads to substantial elongation of this bond (Figure 20).[791,959]

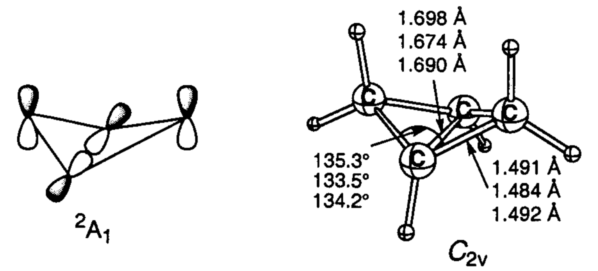
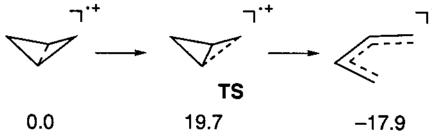


Figure 20. HOMO of bicyclo[1.1.0]butane and the structure of the radical cation at B3LYP (first entry), MP2 (second entry), and QCISD (third entry) with the 6-31G(*d*) basis set.[791]

Scheme 26. Ring Opening of the Bicyclobutane Radical Cation



This radical cation is persistent in a CCl_3F matrix and maintains the C_{2v} symmetry of the parent neutral;[766,960] the rearrangement barrier to the *cis*-butadiene radical cation is $\Delta H^\ddagger = 19.7$ kcal mol^{-1}, and the reaction is -17.9 kcal mol^{-1} exothermic at the CCSD(T)/cc-pVTZ//B3LYP/6-31G(*d*) level in the gas phase (Scheme 26);[791] CCSD(T)/cc-pVTZ//B3LYP/PCM computations in $CHCl_3$ as a model solvent[961] change the geometries of the species and the energetics of this reaction only slightly ($\Delta H^\ddagger = 16.3$ kcal mol^{-1} and $\Delta H_r = -14.9$ kcal mol^{-1}).

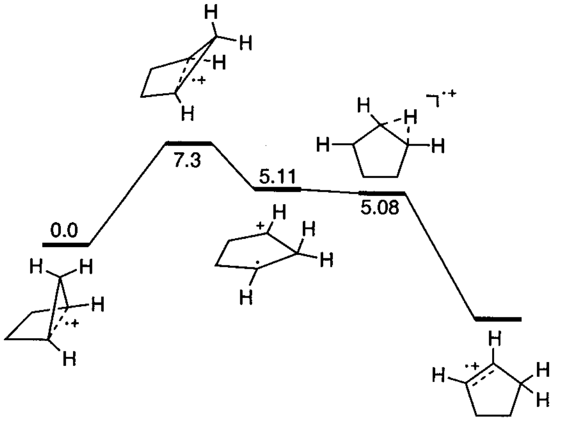
Upon photoinitiation, the rearranged products can re-neutralized through back electron transfer, and a number of such studies were performed for bicyclobutane derivatives.[962–964] The intermediate formation of the substituted bicyclobutane radical cation was proposed as an activation step for the bromination reaction.[965]

4.3.2. Housane

The next bicyclobutane homologue, *housane* (bicyclo[2.1.0]pentane), forms a stable C_s radical cation after SET ionization. A high barrier (23.7 kcal mol^{-1} at CASSCF/6-31G(*d*)) accompanies the interconversion through a planar C_{2v} transition structure.[966] The latter lies in the conical intersection region between the $^2B_1$-ground bonding and the excited $^2A_2$-antibonding states for the planar cyclopentane-1,3-diyl C_{2v} radical cation.[966] The transformation of the housane to the more stable cyclopentene radical cation occurs via the rate-limiting formation of a planar intermediate ($\Delta H^\ddagger = 10.7$ kcal mol^{-1} at CASSCF/6-31G(*d*)) and a subsequent barrierless hydrogen migration.[966] Scheme 27 represents this reaction pathway (at QCISD/6-31G(*d*)//MP2/6-31G(*d*)) which is consistent with the experimentally observed chemical, photochemical,[967] and matrix[968] oxidations of housane.

Substitution[969,970] influences the stability of the housane radical cation strongly: The methyl derivatives are not persistent under matrix conditions[971,972]

Scheme 27. Rearrangement of the Housane Radical Cation (QCISD/6-31G(*d*)//MP2/6-31G(*d*), kcal mol^{-1})



as the planarization barrier is only 3.0 kcal mol^{-1} at QCISD/6-31G(*d*)//MP2/6-31G(*d*) and the 1,2-shift barrier is similarly low (3.4 kcal mol^{-1}).[966] The ring openings of substituted housane radical cations lead to cyclopentenes.[970−973]

4.3.3. [1.1.1]Propellane

The simplest tricyclic hydrocarbon, *[1.1.1]propellane*,[240,974] represents a unique case for a bond between two inverted[975] carbons where the HOMO ($I_p \approx I_a = 9.7$ eV,[976] computed 9.5 eV at MP3/6-311G-(*d*)[977]) describes mainly nonbonding rather than bonding interactions.[976,978−981] As a consequence, ionization leads to a *shortening* of the distance between quaternary carbons in the [1.1.1]propellane radical cation (Figure 21).[977] While being a minimum at the MP2/6-31G(*d*) level, the D_{3h} structure of [1.1.1]-propellane radical cation is a second-order saddle point at the DFT levels and breaks the side C−C bond under the optimizations without symmetry constrains (this work).

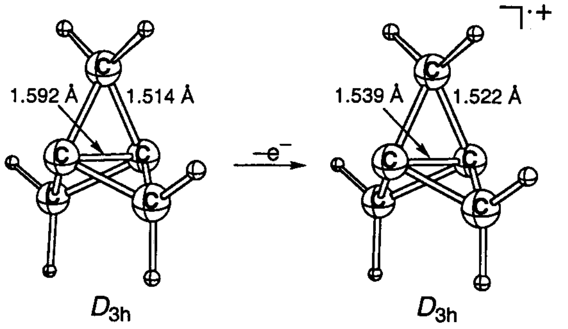


Figure 21. MP2/6-31G(*d*) geometries of [1.1.1]propellane and its radical cation.[977]

4.3.4. Higher Propellanes

The HOMO of *large-ring propellanes* also is located on the central propellanic C−C bond. As it describes strong bonding interactions, ionization leads to C−C bond elongation. The largest elongation (up to 2.208 vs 1.610 Å in the neutral) was found for D_{3h}-symmetric [3.3.3]propellane,[982] in agreement with ESR data (Figure 22).[983]

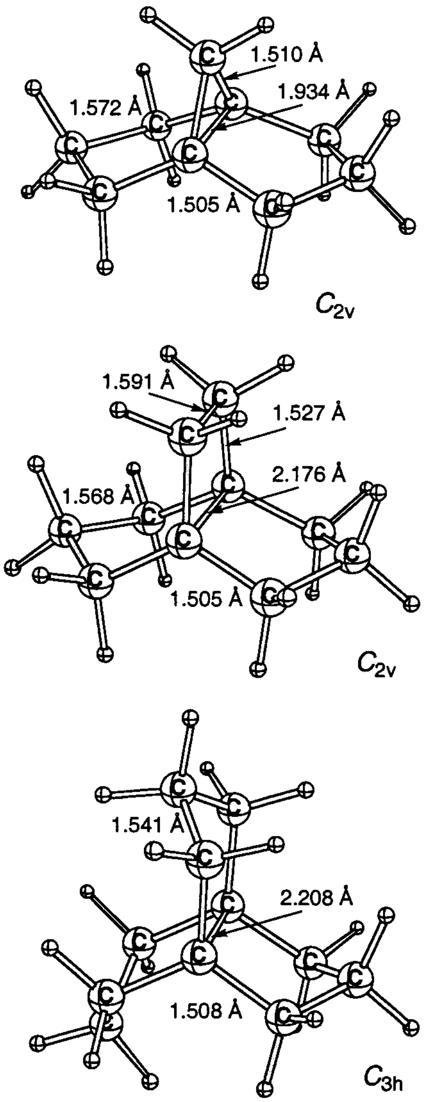


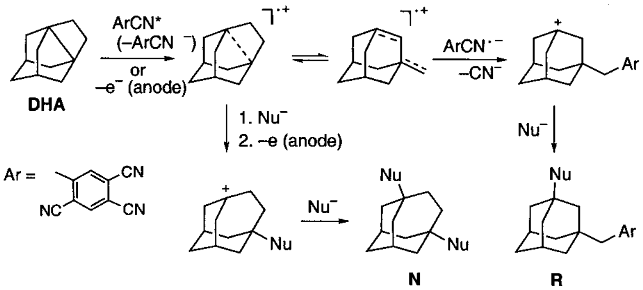
Figure 22. Structures of the [3.3.*n*]propellane ($n = 1, 2, 3$) radical cations at BLYP/6-31G(*d*).[982]

The elongation of the central C−C bond in other [3.3.*n*]propellane radical cations is smaller (from 1.601 to 2.176 Å for [3.3.2]propellane and from 1.537 to 1.934 Å for the [3.3.1]propellane radical cation).[982] Strained propellanes are characterized by a relatively low I_v (8−10 eV); the I_a values usually are 0.8−1.1 eV lower than the I_v due to substantial strain relief after relaxation.[150]

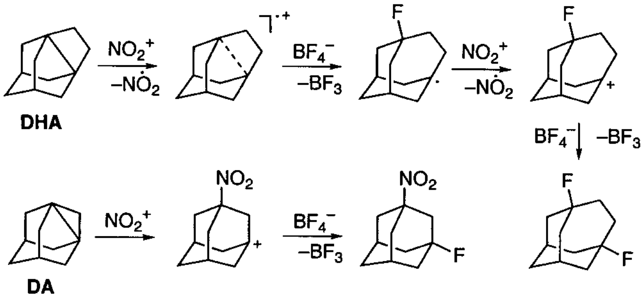
The generation and reactivity of propellane radical cations were studied under anodic[492,984] and photochemical[492,984] oxidation. Scheme 28 summarizes these two reactions for the oxidation of 3,6-dehydrohomoadamantane (**DHA**),[984] where the transformations under one- and two-electron oxidation are entirely different. Under photochemical oxidation conditions an overall one-electron oxidation takes place and the first post-oxidation step involves radical−radical recombination accompanied by rearrangement of the strained cage to form products **R**. Under two-electron anodic oxidation conditions, however, dinucleophilic addition gives products **N** without rearrangement (Scheme 28).

Propellanes undergo oxidative transformations also with metal−oxo reagents[640] and nitrogen-containing

Scheme 28. C−C Bond SET Oxidation in 3,6-Dehydrohomoadamantane



Scheme 29. Electrophilic and Oxidative Activation of C−C Bonds with Nitronium Reagents



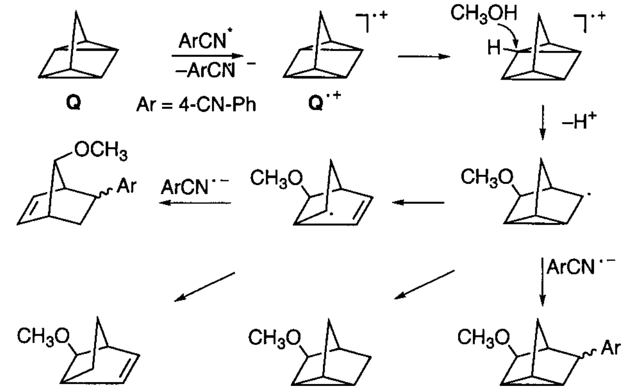
electrophiles.[982,985] A comparative study of the addition reactions to **DHA** and to highly unstable 1,3-dehydroadamantane (**DA**) allow the distinct differentiation between electrophilic and oxidative pathways in the σ_{C-C} activations with electrophiles−oxidizers.[982] Scheme 29 shows that dinucleophilic products are formed from **DHA** with $NO_2^+BF_4^-$ through ET activation, while **DA** forms nitro derivatives after electrophilic attack of NO_2^+.

4.3.5. Quadricyclane

Another highly strained hydrocarbon, *quadricyclane* (**Q**), is of high practical interest because of its possible use in photochemical energy storage applications (equilibrium with norbornadiene).[986,987] The I_v = 7.86 eV of **Q** is extremely low,[988] and the corresponding radical cation **Q**$^{\bullet+}$ isomerizes rapidly in a matrix at 77 K,[988−990] under pulse radiolysis in liquid methylcyclohexane at 133 K[991] and under chemical[992] or electrochemical[993,994] oxidation to the norbornadiene radical cation which is 11 kcal mol^{-1} more stable at CCSD(T)/6-31G(*d*)//MP2/6-31G(*d*).[995] Unrearranged **Q**$^{\bullet+}$ was observed experimentally only with time-resolved ESR spectroscopy.[996] The PES for the rearrangement was explored at MNDO,[988] MP2,[995,997,998] and DFT[997,999] levels of theory with medium-sized (mainly 6-31G(*d*) and 6-31G(*d,p*)) basis sets. The rearrangement occurs as a concerted asynchronous process through a C_s-symmetrical TS. The DFT and QCISD(T) computations largely overestimate the barrier (10.9 kcal mol^{-1} at B3LYP/6-31G(*d*)[997] and 12.0 kcal mol^{-1} at QCISD(T)/6-31G(*d,p*)//MP2/6-31G(*d*)[998]) vs experiment[1000] (4.8 kcal mol^{-1}). Another C_{2v}-symmetrical stationary structure found on the **Q**$^{\bullet+}$ PES is a second-order saddle point.

The photooxidation of **Q** with excited 1,4-dicyanobenzene in the presence of methanol was studied experimentally.[1001−1003] **Q**$^{\bullet+}$ is attacked *exo*-stereospecifically by the nucleophile,[1004] and the radical thus formed rearranges to give aryl-substituted products or methanol adducts (Scheme 30).[1002]

Scheme 30. Stereochemistry of the Quadricyclane Radical Cation Ring Opening in the Presence of a Nucleophile



In the photochemically induced oxidation of **Q** with *p*-quinones, the recombination of the radical ion pair [**Q**$^{\bullet+}$//quinone$^{\bullet-}$] also occurs *exo*-stereoselectively.[1005] An interesting and unique experiment is the generation of triplet biradicals under photoreaction of **Q** with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BDTA) via back electron transfer within the **Q**$^{\bullet+}$/BDTA$^{\bullet-}$ system.[1006] The chemical oxidation/back electron transfer of **Q** with trisarylaminium salts yields norbornadiene exclusively.[992]

4.3.6. Pagodanes

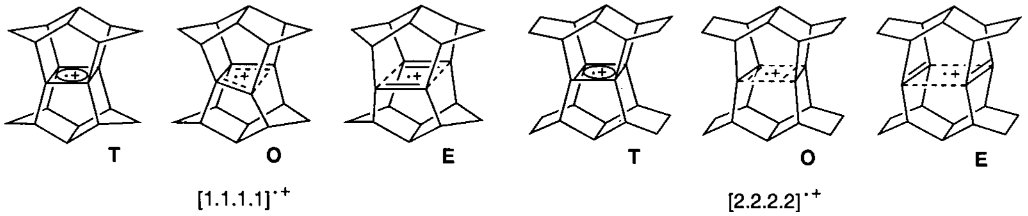
The *pagodanes*, one of the most beautiful families of cage compounds, form relatively stable radical cations with spins and densities located on the central cyclobutane moiety.[1007−1011] Three structures were located for the [1.1.1.1]pagodane radical cation (Scheme 31),[1012] with the “extended” D_{2h} structure **E** with two short (double) and two long CC bonds in the cyclobutane moiety being most stable. The D_{2h} “tight” structure **T** is a transition state for the interconversion of two “open” (**O**) C_{2v} forms which contain a trapezoid cyclobutane moiety. The observed FDMR spectra of the [1.1.1.1]pagodane radical cation[1012] agrees with structure **T**, probably due to fast averaging of **O** forms. Our computations at B3LYP/6-31G(*d*) + ΔZPVE show that **T** and **O** are energetically virtually identical and that **E** is 16.5 kcal mol^{-1} more stable.

The situation with the higher homologue [2.2.2.2]-pagodane (as well as with other members of this family[1013]) is similar: The most stable form is **E**; however, it was pointed out that “*The minima could not be checked by a frequency analysis because of the size of the systems*”. The ESR signals were attributed to a D_{2h} structure of the [2.2.2.2] pagodane radical cation.[1014]

4.3.7. Cubane

The highly symmetrical hydrocarbon *cubane* ($E_{1/2}$ = 1.73 V vs SCE)[994,1015] is kinetically stable because breaking of one of the C−C bonds homolytically or heterolytically causes only minor changes in the rigid cage structure.[1016] Hence, the cubane radical cation

Scheme 31. Tight (T), Opened (O), and Extended (E) Structures of Pagodane-type Radical Cations



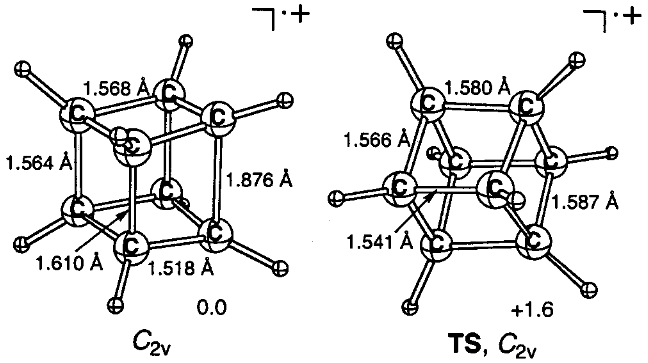
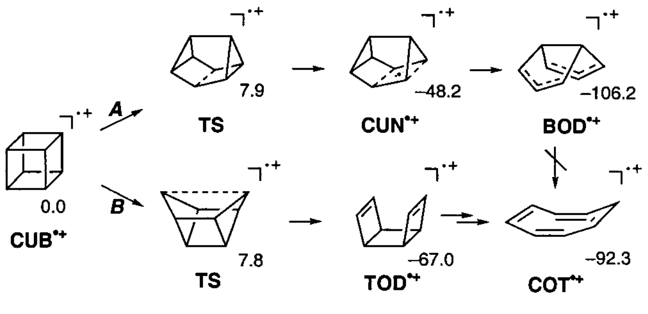


Figure 23. Geometries of the cubane radical cation minimum and the TS (B3LYP/6-31G(*d*); relative energies in kcal mol^{-1} at BCCD(T)/cc-pVDZ//B3LYP/6-31G(*d*)).[792]

(**CUB**$^{\bullet+}$) maintains some structural features of the neutral hydrocarbon but distorts from O_h to C_{2v} symmetry to a structure with one elongated C−C bond (Figure 23).[792]

The interconversion of the 12 degenerate radical cation structures[1017] occurs via a very low barrier (1.6 kcal mol^{-1} at BCCD(T)/cc-pVDZ//B3LYP/6-31G(*d*)),[792] and only the averaged highly symmetrical structure is observed under matrix conditions.[1017,1018] Hydrogen loss from the **CUB**$^{\bullet+}$ is unfavorable because of the instability of the cubyl cation;[1019] rearrangements, on the other hand, are highly exothermic. There are two possible pathways for these: isomerization to the cuneane radical cation (**CUN**$^{\bullet+}$), which was initially proposed (pathway ***A***, Scheme 32),[1018] and fragmentation to the *syn*-tricyclooctadiene radical cation (**TOD**$^{\bullet+}$, pathway ***B***). Both mechanisms were recently computed at the BCCD(T)/cc-pVDZ//B3LYP/6-31G(*d*) level,[792] which shows that **CUB**$^{\bullet+}$ preferentially follows pathway **B**.

Scheme 32. Two Rearrangement Pathways of the Cubane Radical Cation (CUB•$^{+}$)



This fragmentation of **CUB**$^{\bullet+}$ to the cyclooctatetraene radical cation **COT**$^{\bullet+}$ omitting the formation of the cuneane radical cation (**CUN**$^{\bullet+}$) is strongly supported by experimental studies both in solution[792] and under matrix conditions.[1020]

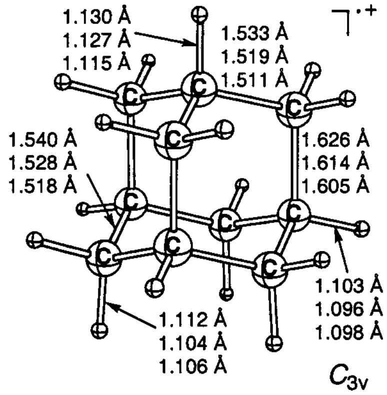


Figure 24. Geometry of the adamantane radical cation at BLYP (first line), B3LYP (second line), and MP2 (third line) with a 6-31G(*d*) basis set.[150,984]

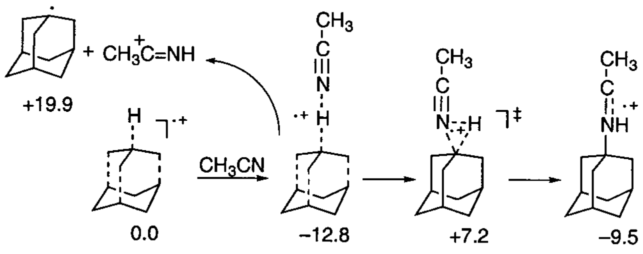
4.3.8. Adamantane

Having a triply degenerate and highly delocalized low-lying HOMO, adamantane, in contrast to cubane, elongates several bonds after SET ionization: the C_{3v} adamantane radical cation (AdH$^{\bullet+}$) displays *three* elongated C−C and *four* long C−H bonds (Figure 24).[150,984]

The fragmentation reaction for AdH$^{\bullet+}$ in the gas phase was computed at MP2/6-31G(*d*) + ΔZPVE. Hydrogen radical loss is energetically (+13.8 kcal mol^{-1}, the barrier is 16.1 kcal mol^{-1}) much less unfavorable than deprotonation (+188.1 kcal mol^{-1}) (Figure 25).[150]

In solution, AdH$^{\bullet+}$ exothermically (−12.8 kcal mol^{-1}, B3LYP/6-31G(*d*)) forms a complex with the solvent (e.g., acetonitrile, Scheme 33 and Figure 26) and one of the C−H bridgehead bonds elongates even more than in the gas phase. The insertion of an acetonitrile molecule into a half-broken C−H bond is exothermic (−9.5 kcal mol^{-1}) but occurs through a high barrier (20 kcal mol^{-1}) via a very late TS (Figure 26). Thus, proton transfer to the solvent dominates for AdH$^{\bullet+}$ in solution.

Scheme 33. Deprotonation Energetics for the Adamantane Radical Cation in Acetonitrile (kcal mol^{-1}, B3LYP/6-31G(*d*))



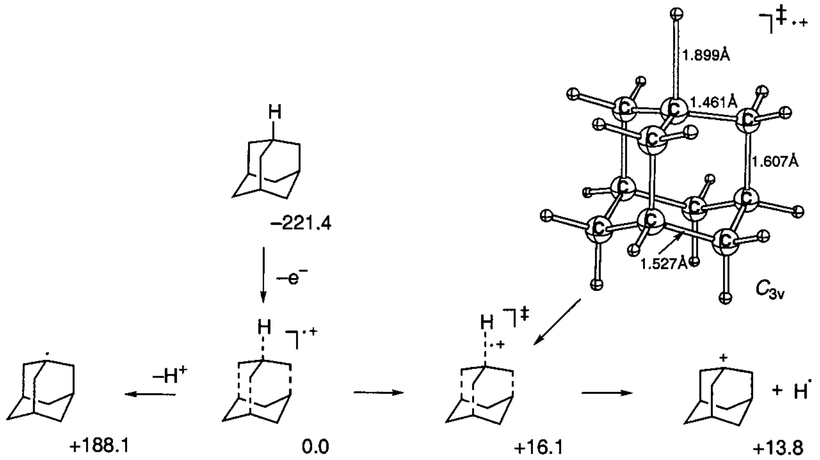


Figure 25. Energetics for hydrogen vs proton loss from the adamantane radical cation (kcal mol^{-1}) and the transition structure for hydrogen loss (gas phase, MP2/6-31G(*d*).[150]

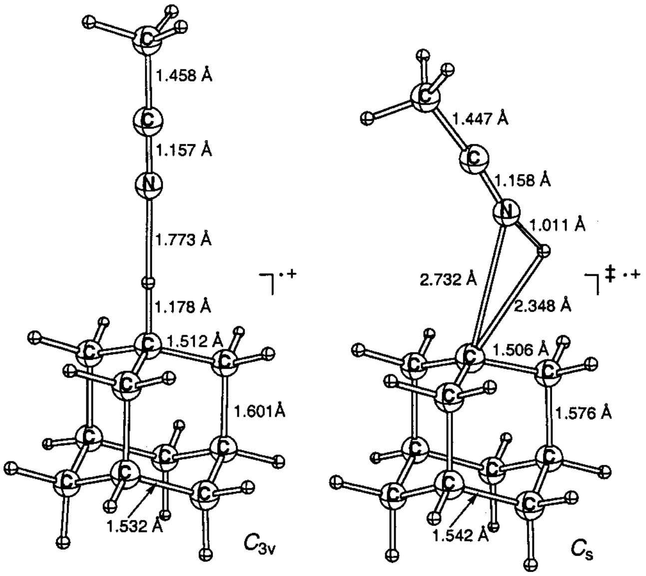
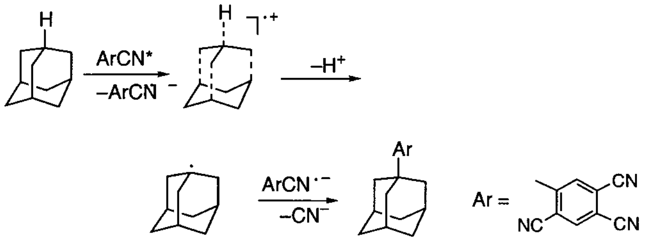


Figure 26. Geometry of the adamantane radical cation complex with an acetonitrile molecule (C_{3v}) and the transition structure for the insertion of acetonitrile into a C−H bond at B3LYP/6-31G(*d*).[150]

The computations identify only one C_{3v}-symmetrical form of the adamantane radical cation both in the gas phase and in the presence of an explicit solvent molecule. This in good agreement with the experimental behavior of AdH$^{\bullet+}$ under electron impact ionization in the gas phase where only the $[M - 2]^+$ ion is formed after the fragmentation of the 1,3,5,7-tetradeuterioadamantane radical cation.[150] An exclusive bridgehead H-elimination is also observed under photooxidation of adamantane with TCB in solution, where only 1-adamantyl radical coupling products form (Scheme 34).[952,1021]

Scheme 34. Selective Deprotonation of the Adamantane Radical Cation upon SET Oxidation



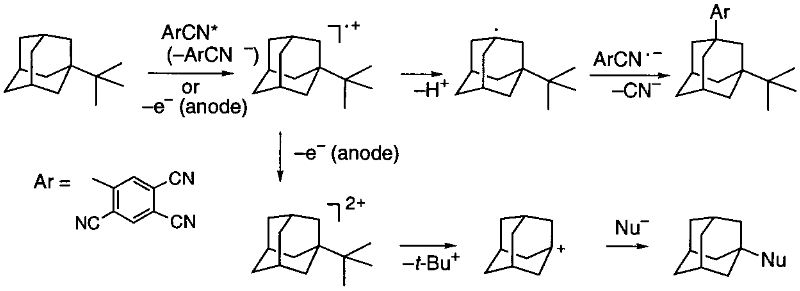
The adamantane radical cation was generated from adamantane by anodic oxidation, and again, only a tertiary substituted product (1-acetamino adamantane) was found.[1022,1023] It is important to note that the behavior of alkyl adamantanes under photoinduced SET (C−H substitution)[1021] and under electro-oxidation (C−C bond fragmentation)[1024,1025] is different. This might be explained by the intermediacy of dications formed after double ET on the anode.[763] These two pathways are depicted in Scheme 35 for *tert*-butyl adamantane as an example.

High 3° selectivities for some adamantane ionic substitutions with electrophiles (polar halogenation,[1026,1027] nitroxylations with anhydrous HNO_3,[1028,1029] activations by NO^+ [1030] or NO_2^+ salts,[818,819,1031] aprotic superacids,[1032] catalytic sulfoxidations with SO_2/O_2,[1033] etc.[1034]) could be attributed to significant ET contributions to the TSs for the C−H activation. Despite the claim that "*Single electron transfer (SET) nitration of adamantane by* NO_2^+ *is unlikely as the first ionization potential of adamantane is high*",[819] eq 32, representing such a reaction, is −24.4 kcal mol^{-1} (B3LYP/6-31G(*d*)) exothermic and electron transfer *is* favorable.[984]

$$\mathrm{AdH} + \mathrm{NO_2}^+ \rightarrow \mathrm{AdH}^{\bullet+} + \mathrm{NO_2}^\bullet \qquad (32)$$

The mechanistic picture for the reactions of oxidizing electrophiles with adamantane and some other cage compounds[1035] probably is very similar to that of aromatics, where an SET activation step involving radical cations[1036] was proposed for NO_2^+ and recently[1037,1038] also for NO^+ reagents.[1039,1040] A similar situation arises for selective 3° substitutions of adamantane with highly electrophilic radicals ($NO_3^\bullet$),[490] metal−oxo reagents $[CrO_2(OCOCF_3)_2]$,[626] palladium acetate systems,[1041,1042] and electrochemically generated high oxidation state iridium species,[1043] where advanced ET from the hydrocarbon moiety to the reagent in the TSs for H-abstraction (vide supra) raises the selectivities substantially.

Scheme 35. Photoinduced SET and Electrochemical Double Oxidation of *tert*-Butyl Adamantane



5. Concluding Remarks

Contrary to popular belief, it is not particularly difficult to activate and functionalize alkanes—regioselectivity is the crux of the problem because the various aliphatic C−H and C−C bonds often have comparable energies and are attacked indiscriminately, leading to product mixtures. The activation takes place either in a concerted fashion through hydrogen-atom abstractions as well as inner-sphere electron transfer or nonconcertedly through single-electron oxidations giving radical cation intermediates.

The selectivities with simple radicals (Hal$^•$, atomic oxygen, HO$^•$, $NO_x^•$, etc.) are generally unappealing: discrimination between primary, secondary, and tertiary positions as well as between C−H and C−C bonds is rather low. Some improvement is achieved if these radicals are produced in the vicinity of a more complex molecular structure (metal-catalyzed oxidations), which probably provides the steric bulk needed for positional discrimination. The same concept can be used to explain the much higher selectivities of bulky radicals such as *t*-BuO$^•$ and $^•CHal_3$. The latter type of radicals can be prepared very conveniently under phase-transfer conditions, and they are more selective toward C−H bonds due to their carbon-centered nature (strained hydrocarbons still undergo C−H activation without fragmentation).

Closed-shell molecules such as dioxirane derivatives and metal−oxo species may also exhibit radical-like behavior and can, hence, be used to functionalize C−H, and, in exceptional cases, of very strained substrates C−C bonds, with pronounced selectivities. However, it cannot be excluded that these and related reactions proceed through nonradical structures (oxenoid insertion). Metal−oxo compounds are also involved in alkane oxidations with cytochrome P450 and methane monooxygenase (MMO); the mechanisms for these types of transformations are complex but all seem to involve highly electrophilic Fe=O species at some stage. The ability of the reagent to activate and polarize the substrate results in extraordinarily high chemo- and regioselectivities.

A very important conclusion is that polar contributions (polarization of the alkane through the reagent) are a requirement for exceptionally high positional selectivities. This is not to say that the activating reagent should be charged (e.g., a strong electrophile), as there also must be a balance between the ability to polarize the hydrocarbon and to remove just one electron in the overall process (a two-electron process would be a purely electrophilic activation leading to cations prone to rearrangements with concomitant loss of selectivity).

As a consequence, polar electrophiles (radicals or closed-shell neutrals) are generally quite selective. There is somewhat of a “gray zone” of inner- and outer-sphere ET reactions: for instance, typical electrophiles such as NO^+, protonated hydrogen peroxide ($H_3O_2^+$), charged $M=O^{n+}$ species, and many others generally resemble C−H or C−C activation transition structures where the hydrocarbon moiety is reminiscent of the free-radical cation. That is, these electrophiles usually form encounter complexes with the alkane and then oxidize the substrate (inner-sphere electron-transfer), followed by internal rearrangement.

Stronger oxidizers actually produce the alkane radical cation which very often distorts (the electron is taken out of one particular σ-bonding orbital) in a rather *predictable* fashion. Hence, the SET oxidations of alkanes with photoexcited aromatics or under anodic conditions are quite selective. Exceptions are very highly strained systems which may undergo rapid rearrangements before nucleophilic trapping (e.g., cubane radical cation).

We view the reactions of radicals, closed-shell electrophiles, and single-electron oxidizers as being of the same general type at different ends of the overall mechanistic spectrum: in all cases, transfer of a partially positively charged polarized hydrogen takes place. (This is also the case in purely electrophilic activations, often referred to as “hydride transfer”.) The selectivity increases in the same direction from radicals to SET oxidizers for relatively unstrained alkanes.

Finally, we note that theory reproduces fundamental radical abstraction reactions very well; relative barriers for H-abstractions typically are in good agreement with experiment. DFT is particularly useful in this context as it includes some of the required electron-correlation effects needed to describe odd-electron systems and does not suffer from many of the drawbacks associated with traditional ab initio methods. Radical cations are far more difficult to describe theoretically, and DFT should be used with caution; traditional methods do not do much better though. Clearly, improved theoretical approaches to treat open-shell, charged species are needed.

Alkane functionalization is a fast developing and vibrant area of chemistry spanning all subdisciplines. This review demonstrates that the fruitful combination of experiment and theory not only is useful but often required to help understand the mechanisms of selective transformations of aliphatics into a large number of useful chemicals.

6. Acknowledgments

This article and a major fraction of our own contributions to the subject have only become possible due to the generous support of the Deutsche Forschungsgemeinschaft, the Ukrainian Science Foundation, the Fonds der Chemischen Industrie, the Volkswagenstiftung, the Alexander-von-Humbold-Stiftung, the Petroleum Research Fund (administered by the American Chemical Society), the NATO Science Program, and the University of Georgia. We are indebted to our co-workers, named in the respective references, for their numerous contributions. We also thank Prof. Dr. Armin de Meijere for his encouragement and interest in the work carried out in Göttingen.

7. Acronyms

//	"at the geometry of"
AIBN	*N*-azoisobutyronitrile
AM1	Austin model 1
BAC	bond additive corrections
B88	Becke's 88 exchange functional
BCCD(T)	Brueckner doubles coupled cluster method, triples included perturbatively
BDE	bond dissociation energy
BDTA	benzophenone tetracarboxylic dianhydride
BHandHLYP	Becke's half-and-half HF with Lee–Yang–Parr correlation
B3LYP	Becke's three-parameter exchange with Lee–Yang–Parr correlation functional
B3P86	Becke's three-parameter exchange with Perdew 86 correlation functional
B3PW91	Becke's three-parameter exchange with Perdew 91 correlation functional
BLYP	Becke's 88 exchange with Lee–Yang–Parr correlation functional
CAN	cerium(IV) ammonium nitrate
CASSCF	complete active space SCF
CCSD	coupled cluster method with single and double excitations
CCSD(T)	coupled cluster, singles and doubles with triples included perturbatively
CI	configuration interaction
m-CPBA	*m*-chlorperbenzoic acid
CUS	canonical unified statistical
CVT	canonical variational transition
Cys	cysteine
D95	Dunning/Huzinaga full double-ζ basis set
DFT	density functional theory
DL	dual level
DMD	dimethyldioxirane
DZ	double-ζ
ECE	electrochemical–chemical–electrochemical
ESR	electron spin resonance
ET	electron transfer
FID	flame ionization detector
G1	Gaussian-1 (theory)
G2	Gaussian-2 (theory)
GC	gas chromatography
HF	Hartree–Fock
HFB	Becke's 88 with Slater exchange
HOMO	highest occupied molecular orbital
IRC	intrinsic reaction coordinate
KIE	kinetic isotope effect
L	ligand
LACVP	Los Alamos effective core potentials DZ
LACV3P	Los Alamos effective core potentials TZ
MD	molecular dynamics
MMO	methane monooxygenase
MNDO	Modified neglect of differential overlap
MP#	Møller–Plesset (order)
MP4SDTQ	MP4 with singles, doubles, triples, and quadruples
MR	multireference
MT	multidimensional tunneling
NBS	*N*-bromo succinimid
μOMT	microcanonical optimized multidimensional tunneling
OS	open shell
PCM	polarized continuum model
PEPICO	photoion coincidence
PES	potential energy surface
PINO	phthalimide-*N*-oxyl
PMP2	spin-projected MP2
PT	phase-transfer
PTC	phase-transfer catalysis
QCISD	quadratic configurational interaction with singles and doubles
QCISD(T)	QCISD with triples included perturbatively
RRKM	Rice–Ramsperger–Kassel–Marcus
SAC	spin-adapted correlation theory
SBK	Stevens–Bash–Krauss effective core potentials DZ
SCE	standard calomel electrode
SCF	self-consistent field
SCRF	self-consistent reaction field
SCT	semiclassical tunneling corrections
SET	single-electron transfer
S_H	substitution homolytic
SHT	synchronous hydride transfer
TCB	tetracyanobenzene
TEMPO	tetramethylpiperidine-*N*-oxide
TS	transition structure
TZ	triple-ζ
TZ2P	triple-ζ with double polarization
TZV	triple-ζ valence
VB	valence bond
cc-pVTZ	correlation consistent valence, polarized triple-ζ
cc-VTZ2P	correlation consistent valence, triple-ζ with double polarization
ZPVE	zero-point vibrational energy

8. References

(1) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970–1973.
(2) Bromberg, S. E.; Yang, W.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260–263.
(3) Huyser, E. S. *Free Radical Chain Reactions*; Wiley-Interscience: New York, 1970.
(4) Poutsma, M. I.; Kochi, K. A. *Free Radicals*; J. Wiley: New York, 1973.
(5) Hoz, S. *Acc. Chem. Res.* **1993**, *26*, 69–74.
(6) Williams, I. H. *Chem. Soc. Rev.* **1993**, *22*, 277–283.
(7) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; John Wiley & Sons: Chichester, 1995.
(8) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411–1456.
(9) Minisci, F. *Substituent effects in free radical chemistry*; Dordrecht, 1986.
(10) Jones, W. D. In *Activation of Unreactive bonds and organic synthesis*; Murai, S., Ed.; Springer: Berlin-Heidelberg-New York-Barcelona-Hong Kong-London-Milan-Paris-Singapore-Tokyo, 1999; pp 10–46.
(11) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879–2932.
(12) Schäfer, H. J. In *The chemistry of alkanes and cycloalkanes*; Patai, S, Rappoport, Z., Eds.; John Wiley & Sons Ltd: Chichester-New York-Brisbane-Toronto-Singapore, 1992; 781–808.

(13) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.

(14) Olah, G. A.; Farooq, O.; Prakash, G. K. S. *Activation and Functionalization of Alkanes*; John Wiley & Sons: New York, 1989.

(15) Hill, C. L. *Activation and Functionalization of Alkanes*; John Wiley & Sons Inc.: New York, 1989.

(16) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245−269.

(17) Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. *Selective Hydrocarbon Activation, Principles and Progress*; VCH: Weinheim, 1990.

(18) Sommer, J.; Bukala, J. *Acc. Chem. Res.* **1993**, *26*, 370−376.

(19) Hill, C. L.; Smegal, J. A.; Henly, T. J. *J. Org. Chem.* **1983**, *48*, 3277−3281.

(20) Crabtree, R. H. "The entire volume 504 of the Journal of Organometallic Chemistry (1995) was dedicated to this research area", 1995.

(21) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987−1007.

(22) Schenk, M.; Smit, B.; Vlugt, T. J. H.; Maesen, T. L. M. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 736−739.

(23) Dugal, M.; Sankar, G.; Raja, R.; Thomas, J. M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2310−2313.

(24) Raja, R.; Sankar, G.; Thomas, J. M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2313−2316.

(25) Milas, I.; Nascimento, M. A. C. *Chem. Phys. Lett.* **2001**, *338*, 67−73.

(26) Blaszkowski, S. R.; Nascimento, M. A. C.; van Santen, R. A. *J. Phys. Chem.* **1996**, *100*, 3463−3472.

(27) Esteves, P. M.; Nascimento, M. A. C.; Mota, C. J. A. *J. Phys. Chem.* **1999**, *103*, 10417−10420.

(28) Boronat, M.; Viruela, P.; Corma, A. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3327−3333.

(29) Okulik, N. B.; Diez, R. P.; Jubert, A. H.; Esteves, P. M.; Mota, C. J. A. *J. Phys. Chem.* **2001**, *105*, 7079−7084.

(30) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437−2450.

(31) Coulston, G. W.; Bare, S. R.; Kung, H.; Birkeland, K.; Bethke, G. K.; Harlow, R.; Herron, N.; Lee, P. L. *Science* **1997**, *275*, 191−193.

(32) Gilbert, T. M.; Hristov, I.; Ziegler, T. *Organometallics* **2001**, *20*, 1183−1189.

(33) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831−10845.

(34) Vidal, V.; Theolier, A.; ThivolleCazat, J.; Basset, J. M. *Science* **1997**, *276*, 99−102.

(35) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4442−4450.

(36) Waltz, K. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 11358−11369.

(37) Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211−213.

(38) Loew, G. H.; Harris, D. L. *Chem. Rev.* **2000**, *100*, 407−419.

(39) Shilov, A. E.; Shteinman, A. A. *Acc. Chem. Res.* **1999**, *32*, 763−771.

(40) Solomon, E. I.; Brunold, T. C.; Davis, M. I.; Kemsley, J. N.; Lee, S.-K.; Lehnert, N.; Neese, F.; Skulan, A. J.; Yang, Y.-S.; Zhou, J. *Chem. Rev.* **2000**, *100*, 235−349.

(41) Ridyard, C. H.; Whittaker, R. A.; Higgins, S. D.; Roberts, S. M.; Willets, A. J.; Bailey, P. D.; Rosair, G. M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1811−1819.

(42) Bailey, P. D.; Higgins, S. D.; Ridyard, C. H.; Roberts, S. M.; Rosair, G. M.; Whittaker, R. A.; Willetts, A. J. *Chem. Commun.* **1996**, 1833−1834.

(43) Goosen, A.; Morgan, D. H. *J. Chem. Soc., Perkin Trans. 2* **1994**, 557−562.

(44) Simon, Y.; Scacchi, G.; Baronnet, F. *Can. J. Chem.* **1996**, *74*, 1391−1402.

(45) Nozaki, C.; Misono, M.; Mizuno, N. *Chem. Lett.* **1998**, 1263−1264.

(46) Ermolenko, L. P.; Giannotti, C. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1205−1210.

(47) Vargaftik, M. N.; Stolyarov, I. P.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1990**, 1049−1050.

(48) Sun, H.; Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1996**, *118*, 6873−6879.

(49) Blatter, F.; Sun, H.; Frei, H. *Chem. Eur. J.* **1996**, *2*, 385−389.

(50) Chen, K.; Iglesia, E.; Bell, A. T. *J. Phys. Chem.* **2001**, *105*, 646−653.

(51) Baird, C. *Environmental Chemistry*; Freeman: New York, 1995.

(52) Crutzen, P. J. *Pure Appl. Chem.* **1998**, *70*, 1319−1326.

(53) Atkinson, R. *Pure Appl. Chem.* **1998**, *70*, 1327−1334.

(54) Atkinson, R. *Pure Appl. Chem.* **1998**, *70*, 1335−1343.

(55) Thompson, A. M. *Isr. J. Chem.* **1994**, *34*, 277−288.

(56) Platt, U.; Heintz, F. *Isr. J. Chem.* **1994**, *34*, 289−300.

(57) Molina, M. J.; Molina, L. T.; Kolb, C. E. *Annu. Rev. Phys. Chem.* **1996**, *47*, 327−367.

(58) Good, D. A.; Kamboures, M.; Santiano, R.; Francisco, J. S. *J. Phys. Chem.* **1999**, *103*, 9230−9240.

(59) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horváth, I. T.; Eller, K. *Organometallics* **1993**, *12*, 895−905.

(60) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−2765.

(61) Jackson, R. A. *Tetrahedron* **1991**, *47*, 6777−6786.

(62) Chandra, A. K.; Uchimaru, T. *J. Phys. Chem.* **2000**, *104*, 9244−9249.

(63) Blowers, P.; Ford, L.; Masel, R. *J. Phys. Chem.* **1998**, *102*, 9267−9277.

(64) Chen, Y.; Tschuikow-Roux, E. *J. Phys. Chem.* **1993**, *97*, 3742−3749.

(65) Wheeler, M. D.; Tsiouris, M.; Lester, M. I.; Lendvay, G. *J. Chem. Phys.* **2000**, *112*, 6590−6602.

(66) Northrop, D. B. *J. Am. Chem. Soc.* **1999**, *121*, 3521−3524.

(67) Kohen, A.; Klinman, J. P. *Acc. Chem. Res.* **1998**, *31*, 397−404.

(68) Senosiain, J. P.; Musgrave, C. B.; Golden, D. M. *J. Phys. Chem.* **2001**, *105*, 1669−1675.

(69) Ichikawa, T.; Kagei, K.; Tachikawa, H.; Ishitani, Y. *J. Phys. Chem.* **1999**, *103*, 6288−6294.

(70) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401−408.

(71) Bockman, T. M.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 2826−2830.

(72) Albini, A.; Mella, M.; Freccero, M. *Tetrahedron* **1994**, *50*, 575−607.

(73) Anne, A.; Fraoua, S.; Hapiot, P.; Moiroux, J.; Savèant, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 7412−7421.

(74) Parker, V. D.; Chao, E. T.; Zheng, G. *J. Am. Chem. Soc.* **1997**, *119*, 11390−11394.

(75) Parker, V. D.; Zhao, Y. X.; Lu, Y.; Zheng, G. *J. Am. Chem. Soc.* **1998**, *120*, 12720−12727.

(76) Cheng, T.-Y.; Bullock, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3150−3155.

(77) Nesheim, J. C.; Lipscomb, J. D. *Biochemistry* **1996**, *35*, 10240−10247.

(78) Rickert, K. W.; Klinman, J. P. *Biochemistry* **1999**, *38*, 12218−12228.

(79) Fast, P. L.; Corchado, J. C.; Truhlar, D. G. *J. Chem. Phys.* **1998**, *109*, 6237−6245.

(80) Corchado, J. C.; Truhlar, D. G.; Espinosa-Garcia, J. *J. Chem. Phys.* **2000**, *112*, 9375−9389.

(81) Harry, C.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **1999**, *31*, 425−431.

(82) Luo, N.; Kombo, D. C.; Osman, R. *J. Phys. Chem.* **1997**, *101*, 926−936.

(83) Cohen, N. *Int. J. Chem. Kinet.* **1991**, *23*, 683−700.

(84) Snelgrove, D. W.; Lusztyk, J.; Banks, J. T.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469−477.

(85) Denisov, E. T. *Russ. Chem. Rev.* **1997**, *66*, 953−971.

(86) Héberger, K. *J. Phys. Org. Chem.* **1994**, *7*, 244−250.

(87) Ma, X. L.; Schobert, H. H. *Ind. Eng. Chem. Res.* **2001**, *40*, 743−750.

(88) Zavitsas, A. A. *J. Chem. Soc., Perkin Trans. 2* **1996**, 391−393.

(89) Zavitsas, A. A. *J. Chem. Soc., Perkin Trans. 2* **1998**, 499−502.

(90) Nau, W. M. *J. Phys. Org. Chem.* **1997**, *10*, 445−455.

(91) Zavitsas, A. A. *J. Am. Chem. Soc.* **1998**, *120*, 6578−6586.

(92) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1992**, *24*, 983−989.

(93) Roberts, B. P.; Steel, A. J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2155−2162.

(94) Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2719−2725.

(95) Truong, T. N. *J. Chem. Phys.* **2000**, *113*, 4957−4964.

(96) Bally, T.; Borden, W. T. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: Weinheim, 1999; Vol. 13, pp 1−97.

(97) Sana, M.; Leroy, G.; Villaveces, J. L. *Theor. Chim. Acta.* **1984**, *65*, 109−125.

(98) Cremer, D. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; John Wiley & Sons: Chichester, 1998; Vol. 3, pp 1706−1735.

(99) Hiberty, P. C.; Humbel, S.; Danovich, D.; Shaik, S. *J. Am. Chem. Soc.* **1995**, *117*, 9003−9011.

(100) Kobayashi, Y.; Kamiya, M.; Hirao, K. *Chem. Phys. Lett.* **2000**, *319*, 695−700.

(101) Schlegel, H. B. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P., Schaefer, H. F., III, Schreiner, P. R., Eds.; John Wiley & Sons: Chichester, 1998; Vol. 4, pp 2665−2671.

(102) Chuang, Y.-Y.; Coitiño, E. L.; Truhlar, D. G. *J. Phys. Chem.* **2000**, *104*, 446−450.

(103) Basch, H.; Musaev, D. G.; Mogi, K.; Morokuma, K. *J. Phys. Chem.* **2001**, *105*, 3615−3622.

(104) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem.* **2001**, *105*, 2936−2941.

(105) Chandra, A. K.; Uchimaru, T.; Sugie, M.; Sekiya, A. *Chem. Phys. Lett.* **2000**, *318*, 69−74.

(106) Chandra, A. K.; Uchimaru, T. *Chem. Phys. Lett.* **2001**, *334*, 200−206.

(107) El-Taher, S. *Int. J. Quantum Chem.* **2001**, *84*, 426−440.

(108) Schipper, P. R. T.; Gritsenko, O. V.; Baerends, E. J. *J. Chem. Phys.* **1999**, *111*, 4056−4067.

(109) Jursic, B. S. *Chem. Phys. Lett.* **1996**, *256*, 603−608.
(110) Susnow, R. G.; Dean, A. M.; Green, W. H., Jr. *Chem. Phys. Lett.* **1999**, *312*, 262−268.
(111) Espinosa-Garcia, J.; Corchado, J. C.; Truhlar, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 9891−9896.
(112) Siegbahn, P. E. M.; Crabtree, R. H. *Struct. Bonding* **2000**, *97*, 125−144.
(113) Friesner, R. A.; Dunietz, B. D. *Acc. Chem. Res.* **2001**, *34*, 351−358.
(114) Su, M.-D.; Chu, S.-Y. *Int. J. Quantum Chem.* **1998**, *70*, 961−971.
(115) Schröder, D.; Shaik, S.; Schwarz, H. *Acc. Chem. Res.* **2000**, *33*, 139−145.
(116) Harris, N.; Shaik, S.; Schröder, D.; Schwarz, H. *Helv. Chim. Acta* **1999**, *82*, 1784−1797.
(117) Filatov, M.; Shaik, S. *J. Phys. Chem.* **1998**, *102*, 3835−3846.
(118) Ogliaro, F.; de Visser, S. P.; Groves, J. T.; Shaik, S. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2874−2878.
(119) Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *108*, 2545−2555.
(120) Jursic, B. S. *J. Mol. Struct. (THEOCHEM)* **2000**, *499*, 223−231.
(121) Masgrau, L.; Gonzalez-Lafont, A.; Lluch, J. M. *J. Chem. Phys.* **2001**, *115*, 4515−4526.
(122) Yu, H. G. *Chem. Phys. Lett.* **2000**, *332*, 538−544.
(123) Sutherland, J. W.; Su, M. C.; Michael, J. V. *Int. J. Chem. Kinet.* **2001**, *33*, 669−684.
(124) Yu, X.; Li, S.-M.; Xu, Z.-F.; Li, Z.-S.; Sun, C.-C. *J. Mol. Struct. (THEOCHEM)* **2001**, *571*, 71−82.
(125) Lucarini, M.; Pedulli, G. F.; Valgimigli, L. *J. Org. Chem.* **1998**, *63*, 4497−4499.
(126) Merényi, G.; Lind, J. *J. Am. Chem. Soc.* **1994**, *116*, 7872−7876.
(127) Valgimigli, L.; Banks, J. T.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 9966−9971.
(128) Shinohara, H.; Imamura, A.; Masuda, T.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 974−979.
(129) Shaik, S.; Wu, W.; Dong, K. M.; Song, L. C.; Hiberty, P. C. *J. Phys. Chem.* **2001**, *105*, 8226−8235.
(130) Zavitsas, A. A.; Melikian, A. A. *J. Am. Chem. Soc.* **1975**, *97*, 2757−2763.
(131) Roberts, B. P. *Chem. Soc. Rev.* **1999**, *28*, 25−35.
(132) Zavitsas, A. A.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1995**, *117*, 10645−10654.
(133) Levin, Y. A.; Abulkanov, A. G. *Zhurn. Org. Khim.* **1980**, *16*, 480−495.
(134) Heidbrink, J. L.; Ramírez-Arizmendi, L. E.; Thoen, K. K.; Guler, L.; Kenttämaa, H. I. *J. Phys. Chem.* **2001**, *105*, 7875−7884.
(135) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363−370.
(136) Pross, A.; Yamataka, H.; Nagase, S. *J. Phys. Org. Chem.* **1991**, *4*, 135−140.
(137) Reddy, A. C.; Danovich, D.; Ioffe, A.; Shaik, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1525−1539.
(138) Mestres, J.; Hiberty, P. C. *New J. Chem.* **1996**, *20*, 1213−1219.
(139) Handoo, K. L.; Cheng, J.-P.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 5067−5072.
(140) Collins, S. J.; O'Malley, P. J. *Chem. Phys. Lett.* **1995**, *246*, 555−561.
(141) Roth, J. P.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 5486−5498.
(142) Boronat, M.; Viruela, P.; Corma, A. *J. Phys. Chem.* **1997**, *101*, 10069−10074.
(143) Kazansky, V. B.; Frash, M. V.; van Santen, R. A. *Catal. Lett.* **1997**, *48*, 61−67.
(144) Frash, M. V.; Solkan, V. N.; Kazansky, V. B. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 515−520.
(145) Boronat, M.; Viruela, P.; Corma, A. *J. Phys. Chem.* **1999**, *103*, 7809−7821.
(146) Crestoni, M. E.; Fornarini, S.; Lentini, M.; Speranza, M. *J. Phys. Chem.* **1996**, *100*, 8285−8294.
(147) Mestres, J.; Lledós, A.; Duran, M.; Bertrán, J. *J. Mol. Struct. (THEOCHEM)* **1992**, *260*, 259−272.
(148) Fradera, X.; Duran, M.; Mestres, J. *Can. J. Chem.* **2000**, *78*, 328−337.
(149) Apeloig, Y.; Merin-Aharoni, O.; Danovich, D.; Ioffe, A.; Shaik, S. *Isr. J. Chem.* **1993**, *33*, 387−402.
(150) Fokin, A. A.; Schreiner, P. R.; Gunchenko, P. A.; Peleshanko, S. A.; Shubina, T. E.; Isaev, S. D.; Tarasenko, P. V.; Kulik, N. I.; Schiebel, H.-M.; Yurchenko, A. G. *J. Am. Chem. Soc.* **2000**, *122*, 7317−7326.
(151) Decornez, H.; Hammes-Schiffer, S. *J. Phys. Chem.* **2000**, *104*, 9370−9384.
(152) Hammes-Schiffer, S. *Acc. Chem. Res.* **2001**, *34*, 273−281.
(153) Cukier, R. I.; Nocera, D. G. *Annu. Rev. Phys. Chem.* **1998**, *49*, 337−369.
(154) Binstead, R. A.; Stultz, L. K.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 546−551.
(155) Farrer, B. T.; Thorp, H. H. *Inorg. Chem.* **1999**, *38*, 2497−2502.
(156) Soudackov, A.; Hammes-Schiffer, S. *J. Am. Chem. Soc.* **1999**, *121*, 10598−10607.
(157) Fukuzumi, S.; Kitano, T.; Ishikawa, M. *J. Am. Chem. Soc.* **1990**, *112*, 5631−5632.
(158) Baciocchi, E.; D'Acunzo, F.; Galli, C.; Lanzalunga, O. *J. Chem. Soc., Perkin Trans. 2* **1996**, 133−140.
(159) Ishikawa, M.; Fukuzumi, S. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3531−3536.
(160) Verhoeven, J. W.; van Gerresheim, W.; Martens, F. M.; van der Kerk, S. M. *Tetrahedron* **1986**, *42*, 975−992.
(161) Fukuzumi, S.; Ishikawa, M.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1811−1816.
(162) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305−316.
(163) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience: New York, 1987.
(164) Olah, G. A.; Molnár, A. *Hydrocarbon Chemistry*; John Wiley & Sons: New York, 1995.
(165) Olah, G. A. *Acc. Chem. Res.* **1987**, *20*, 422−428.
(166) Sommer, J.; Hachoumy, M.; Culmann, J. C.; Bukala, J. *New J. Chem.* **1997**, *21*, 939−944.
(167) Sommer, J.; Jost, R. *Pure Appl. Chem.* **2000**, *72*, 2309−2318.
(168) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162.
(169) Zhidomirov, G. M.; Avdeev, V. I.; Zhanpeisov, N. U.; Zakharov, I. I.; Yudanov, I. V. *Catal. Today* **1995**, *24*, 383−387.
(170) Maravin, G. B.; Avdeev, M. V.; Bagrii, E. I. *Pet. Chem.* **2000**, *40*, 1−18.
(171) Jia, C. G.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633−639.
(172) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374−6375.
(173) Dinh, L. V.; Gladysz, J. A. *Tetrahedron Lett.* **1999**, *40*, 8995−8998.
(174) Sugawara, K. I.; Ito, F.; Nakanaga, T.; Takeo, H.; Matsumura, C. *J. Chem. Phys.* **1990**, *92*, 5328−5337.
(175) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F. Jr.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 1125−1568.
(176) Wallington, T. J.; Hurley, M. D. *Int. J. Chem. Kinet.* **1993**, *25*, 819−824.
(177) Persky, A. *J. Phys. Chem.* **1996**, *100*, 689−693.
(178) Davis, L. P.; Burggraf, L. W.; Gordon, M. S.; Baldridge, K. K. *J. Am. Chem. Soc.* **1985**, *107*, 4415−4419.
(179) Corchado, J. C.; Espinosa-Garcia, J. *J. Chem. Phys.* **1996**, *105*, 3152−3159.
(180) Louis, F.; Sawerysyn, J.-P. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1437−1445.
(181) Louis, F.; Talhaoui, A.; Sawerysyn, J.-P.; Rayez, M.-T.; Rayez, J.-C. *J. Phys. Chem.* **1997**, *101*, 8503−8507.
(182) Sehested, J.; Bilde, M.; Møgelberg, T.; Wallington, T. J.; Nielsen, O. J. *J. Phys. Chem.* **1996**, *100*, 10989−10998.
(183) Bilde, M.; Sehested, J.; Nielsen, O. J.; Wallington, T. J. *J. Phys. Chem.* **1997**, *101*, 5477−5488.
(184) Whitman, G. M.; US Patent 2,046,090, 1951.
(185) Louis, F.; Rayez, M.-T.; Rayez, J.-C.; Sawerysyn, J.-P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 383−389.
(186) Bottoni, A.; Poggi, G. *J. Mol. Struct. (THEOCHEM)* **1995**, *337*, 161−172.
(187) Maricq, M. M.; Szente, J. J. *J. Phys. Chem.* **1994**, *98*, 2078−2082.
(188) Dumas, J. B. *Liebigs Ann.* **1840**, *33*, 187−191.
(189) Jobson, B. T.; Niki, H.; Yokouchi, Y.; Bottenheim, J.; Hopper, F.; Leaitch, R. *J. Geophys. Res.* **1994**, *99*, 25355−25368.
(190) Keene, W. C.; Jacob, D. J.; Fan, S. M. *Atmos. Environ.* **1996**, *30*, R1−R3.
(191) Graedel, T. E.; Keene, W. C. *Pure Appl. Chem.* **1996**, *68*, 1689−1697.
(192) Truong, T. N.; Truhlar, D. G.; Baldridge, K. K.; Gordon, M. S.; Steckler, R. *J. Chem. Phys.* **1989**, *90*, 7137−7142.
(193) Roberto-Neto, O.; Coitiño, E. L.; Truhlar, D. G. *J. Phys. Chem.* **1998**, *102*, 4568−4578.
(194) Dobbs, K. D.; Dixon, D. A. *J. Phys. Chem.* **1994**, *98*, 12584−12589.
(195) Duncan, W. T.; Truong, T. N. *J. Chem. Phys.* **1995**, *103*, 9642−9652.
(196) Zahniser, M. S.; Berquist, B. M.; Kaufman, F. *Int. J. Chem. Kinet.* **1978**, *10*, 15−29.
(197) Michelsen, H. A. *Acc. Chem. Res.* **2001**, *34*, 331−337 and references therein.
(198) Gonzalez-Lafont, A.; Truong, T. N.; Truhlar, D. G. *J. Chem. Phys.* **1991**, *95*, 8875−8894.
(199) Michelsen, H. A.; Simpson, W. R. *J. Phys. Chem.* **2001**, *105*, 1476−1488.
(200) Chiltz, G.; Goldfinger, P.; Huybrechts, G.; Johnston, H. S.; Meyers, L.; Verbeke, G.; Eckling, R. *J. Chem. Phys.* **1963**, *38*, 1053−1061.
(201) Clyne, M. A. A.; Walker, R. F. *J. Chem. Soc., Faraday Trans.* **1973**, 1547−1567.
(202) Matsumi, Y.; Izumi, K.; Skorokhodov, V.; Kawasaki, M.; Tanaka, N. *J. Phys. Chem.* **1997**, *101*, 1216−1221.
(203) Wiberg, K. B.; Motell, E. L. *Tetrahedron* **1963**, *19*, 2009−2023.
(204) Wallington, T. J.; Hurley, M. D. *Chem. Phys. Lett.* **1992**, *189*, 437−442.

(205) Kaiser, E. W.; Rimai, L.; Schwab, E.; Lim, E. C. *J. Phys. Chem.* **1992**, *96*, 303−306.
(206) Dobis, O.; Benson, S. W. *J. Am. Chem. Soc.* **1991**, *113*, 6377−6386.
(207) Dahl, I. M.; Myhrvold, E. M.; Olsbye, U.; Rohr, F.; Rokstad, O. A.; Swang, O. *Ind. Eng. Chem. Res.* **2001**, *40*, 2226−2235.
(208) Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Dill, M.; Kaiser, E. W. *Int. J. Chem. Kinet.* **1997**, *29*, 43−55.
(209) Wallington, T. J.; Skewes, L. M.; Siegl, W. O.; Wu, C.-H.; Japar, S. M. *Int. J. Chem. Kinet.* **1988**, *20*, 867−875.
(210) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1985**, *17*, 33−41.
(211) Blank, D. A.; Hemmi, N.; Suits, A. G.; Lee, Y. T. *Chem. Phys.* **1998**, *231*, 261−278.
(212) Lewis, R. S.; Sander, S. P.; Wagner, S.; Watson, R. T. *J. Phys. Chem.* **1980**, *84*, 2009−2015.
(213) Stutz, J.; Ezell, M. J.; Ezell, A. A.; Finlayson-Pitts, B. J. *J. Phys. Chem.* **1998**, *102*, 8510−8519.
(214) Varley, D. F.; Dagdigian, P. J. *J. Phys. Chem.* **1996**, *100*, 4365−4374.
(215) Hemmi, N.; Suits, A. G. *J. Chem. Phys.* **1998**, *109*, 5338−5343.
(216) Dobis, O.; Benson, S. W. *J. Phys. Chem.* **2000**, *104*, 5503−5510.
(217) Tschuikow-Roux, E.; Yano, T.; Niedzielski, J. *J. Phys. Chem.* **1984**, *88*, 1408−1414.
(218) Talhaoui, A.; Louis, F.; Devolder, P.; Meriaux, B.; Sawerysyn, J.-P.; Rayez, M.-T.; Rayez, J.-C. *J. Phys. Chem.* **1996**, *100*, 13531−13538.
(219) Talhaoui, A.; Louis, F.; Meriaux, B.; Devolder, P.; Sawerysyn, J.-P. *J. Phys. Chem.* **1996**, *100*, 2107−2113.
(220) Hooshiyar, P. A.; Niki, H. *Int. J. Chem. Kinet.* **1995**, *27*, 1197−1206.
(221) Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1995**, *27*, 613−622.
(222) Tanner, D. D.; Oumar-Mahamat, H.; Meintzer, C. P.; Tsai, E. C.; Lu, T. T.; Yang, D. *J. Am. Chem. Soc.* **1991**, *113*, 5397−5402.
(223) Dneprovskii, A. S.; Kuznetsov, D. V.; Eliseenkov, E. V.; Fletcher, B.; Tanko, J. M. *J. Org. Chem.* **1998**, *63*, 8860−8864.
(224) Rayez, M.-T.; Rayez, J.-C.; Sawerysyn, J.-P. *J. Phys. Chem.* **1994**, *98*, 11342−11352.
(225) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120−5127.
(226) Rosenman, E.; McKee, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 9033−9038.
(227) Xiao, J.-F.; Li, Z.-S.; Ding, Y.-H.; Liu, J.-Y.; Huang, X.-R.; Sun, C.-C. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3955−3960.
(228) Wallington, T. J.; Hurley, M. D. *Chem. Phys. Lett.* **1992**, *194*, 309−312.
(229) Parmar, S. S.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 57−61.
(230) Roberts, J. D.; Dirstine, P. H. *J. Am. Chem. Soc.* **1945**, *67*, 1281−1283.
(231) Cadman, P.; Kirk, A. W.; Trotman-Dickenson, A. F. *J. Chem. Soc., Faraday Trans.* **1976**, 1027−1032.
(232) Walling, C.; Fredricks, P. S. *J. Am. Chem. Soc.* **1962**, *84*, 3326−3331.
(233) Tanko, J. M.; Suleman, N. K. *J. Am. Chem. Soc.* **1994**, *116*, 5162−5166.
(234) Walton, J. C. *Acc. Chem. Res.* **1998**, *31*, 99−107.
(235) Sedlacek, A. J.; Mansueto, E. S.; Wight, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 6223−6229.
(236) Tague, T. J., Jr.; Wight, C. A. *J. Phys. Chem.* **1993**, *97*, 3266−3269.
(237) Ashton, D. S.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 965−967.
(238) Ashton, D. S.; Singh, H.; Tedder, J. M.; Walton, J. C.; Watt, E. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 125−128.
(239) Sedlacek, A. J.; Wight, C. A. *J. Chem. Phys.* **1988**, *88*, 2847−2848.
(240) Levin, M. D.; Kaszynski, P.; Michl, J. *Chem. Rev.* **2000**, *100*, 169−234.
(241) Eaton, P. E.; Temme, G. H., III *J. Am. Chem. Soc.* **1973**, *95*, 7508−7510.
(242) Christl, M. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press Ltd.: London, 1995; Vol. 4, pp 163−224.
(243) Della, E. W.; Head, N. J.; Mallon, P.; Walton, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 10730−10738.
(244) Chen, Y. H.; Tschuikow-Roux, E.; Rauk, A. *J. Phys. Chem.* **1991**, *95*, 9832−9836.
(245) Chen, Y. H.; Rauk, A.; Tschuikow-Roux, E. *J. Phys. Chem.* **1991**, *95*, 9900−9908.
(246) Alfassi, Z. B.; Huie, R. E.; Mittal, J. P.; Neta, P.; Shoute, L. C. T. *J. Phys. Chem.* **1993**, *97*, 9120−9123.
(247) Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092−3099.
(248) Russell, G. A.; Seetula, J. A.; Timonen, R. S.; Gutman, D.; Nava, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3084−3091.
(249) Guha, S.; Francisco, J. S. *J. Mol. Struct. (THEOCHEM)* **2001**, *573*, 171−180.
(250) Amphlett, J. C.; Whittle, E. *Trans. Faraday Soc.* **1968**, *64*, 2130−2142.
(251) Tschuikow-Roux, E.; Salomon, D. R. *J. Phys. Chem.* **1987**, *91*, 699−702.
(252) Miyokawa, K.; Tschuikow-Roux, E. *J. Phys. Chem.* **1992**, *96*, 7328−7331.
(253) Eckstein, B. H.; Sheraga, H. A.; van Artsdalen, E. R. *J. Chem. Phys.* **1954**, *22*, 28−35.
(254) Fettis, G. C.; Knox, J. H.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1960**, *82*, 4177−4185.
(255) Tabushi, I.; Hamuro, J.; Oda, R. *J. Am. Chem. Soc.* **1967**, *89*, 7127−7128.
(256) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162−2169.
(257) Korth, H.-G.; Lange, F.; Lübbe, F.; Müller, W.; Seidel, M.; Sustmann, R. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1293−1297.
(258) Danovich, D.; Apeloig, Y.; Shaik, S. *J. Chem. Soc., Perkin Trans. 2* **1993**, 321−330.
(259) Miyokawa, K.; Ozaki, S.; Yano, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 869−873.
(260) Miyokawa, K.; Tschuikow-Roux, E. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1−5.
(261) Tanner, D. D.; Ochiai, T.; Pace, T. *J. Am. Chem. Soc.* **1975**, *97*, 6162−6165.
(262) Maynes, G. G.; Applequist, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 856−861.
(263) Hoffmann, J. M.; Graham, K. J.; Rowell, C. F. *J. Org. Chem.* **1975**, *40*, 3005−3010.
(264) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493−532.
(265) Tanko, J. M.; Suleman, N. K.; Hulvey, G. A.; Park, A.; Powers, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 4520−4526.
(266) Tanko, J. M.; Mas, R. H.; Suleman, N. K. *J. Am. Chem. Soc.* **1990**, *112*, 5557−5562.
(267) Fokin, A. A.; Lauenstein, O.; Gunchenko, P. A.; Schreiner, P. R. *J. Am. Chem. Soc.* **2001**, *123*, 1842−1847.
(268) Warner, P.; LaRose, R.; Schleis, T. *Tetrahedron Lett.* **1976**, 4443−4446.
(269) Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1252−1254.
(270) Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1371−1376.
(271) Burcat, A.; Dixon-Lewis, G.; Frenklach, M.; Gardiner, W. C., Jr.; Hanson, R. K.; Salimian, S.; Troe, J.; Warnatz, J.; Zellner, R. *Combustion Chemistry, 1984*; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984.
(272) Sutherland, J. W.; Michael, J. V.; Klemm, R. B. *J. Phys. Chem.* **1986**, *90*, 5941−5945.
(273) Tsurumaki, H.; Fujimura, Y.; Kajimoto, O. *J. Chem. Phys.* **2000**, *112*, 8338−8346.
(274) Cohen, N.; Westberg, K. R. *Int. J. Chem. Kinet.* **1986**, *18*, 99−140.
(275) Corchado, J. C.; Espinosa-Garcia, J.; Roberto-Neto, O.; Chuang, Y.-Y.; Truhlar, D. G. *J. Phys. Chem.* **1998**, *102*, 4899−4910.
(276) Espinosa-Garcia, J.; Garcia-Bernaldez, J. C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2345−2351.
(277) Herron, J. T.; Huie, R. E. *J. Phys. Chem.* **1969**, *73*, 3327−3337.
(278) Andresen, P.; Luntz, A. C. *J. Chem. Phys.* **1980**, *72*, 5842−5850.
(279) Miyoshi, A.; Yamauchi, N.; Matsui, H. *J. Phys. Chem.* **1996**, *100*, 4893−4899.
(280) Kreye, W. C. *Chem. Phys. Lett.* **1996**, *256*, 383−390.
(281) Kreye, W. C.; Seybold, P. G. *Chem. Phys. Lett.* **2001**, *335*, 257−264.
(282) Mehandru, S. P.; Anderson, A. B.; Brazdil, J. F. *J. Am. Chem. Soc.* **1988**, *110*, 1715−1719.
(283) Hutchings, G. J.; Scurrell, M. S.; Woodhouse, J. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1388−1389.
(284) Driscoll, D. J.; Martir, W.; Wang, J.-X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 58−63.
(285) Goto, A.; Aika, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 95−98.
(286) Ito, T.; Lunsford, J. H. *Nature* **1985**, *314*, 721−722.
(287) Yamaguchi, Y.; Nagasawa, Y.; Shimomura, S.; Tabata, K. *Int. J. Quantum Chem.* **1999**, *74*, 423−433.
(288) Orlando, R.; Millini, R.; Perego, G.; Dovesi, R. *J. Mol. Catal.* **1997**, *119*, 253−262.
(289) Lee, J.; Grabowski, J. J. *Chem. Rev.* **1992**, *92*, 1611−1647.
(290) Carpenter, M. A.; Farrar, J. M. *J. Chem. Phys.* **1997**, *106*, 5951−5960.
(291) Arnold, S. T.; Morris, R. A.; Viggiano, A. A. *J. Phys. Chem.* **1998**, *102*, 1345−1348.
(292) Yamaguchi, Y.; Nagasawa, Y.; Murakami, A.; Tabata, K. *Int. J. Quantum Chem.* **1998**, *69*, 669−678.
(293) Viggiano, A. A.; Morris, R. A.; Deakyne, C. A.; Dale, F.; Paulson, J. F. *J. Phys. Chem.* **1990**, *94*, 8193−8197.
(294) Neeb, P. *J. Atmos. Chem.* **2000**, *35*, 295−315.
(295) Bott, J. F.; Cohen, N. *Int. J. Chem. Kinet.* **1991**, *23*, 1075−1094.
(296) Finlayson-Pitts, B. J.; Pitts, N. *Atmospheric Chemistry: Fundamentals and Experimental Techniques.*; Wiley-Interscience: New York, 1986.
(297) Jeong, K.-M.; Kaufman, F. *J. Phys. Chem.* **1982**, *86*, 1808−1815.
(298) DeMore, W. B. *J. Phys. Chem.* **1996**, *100*, 5813−5820.
(299) Jursic, B. S. *Int. J. Quantum Chem.* **1997**, *65*, 75−82.

(300) Melissas, V. S.; Truhlar, D. G. *J. Chem. Phys.* **1993**, *99*, 1013–1027.

(301) Gordon, M. S.; Truhlar, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 5412–5419.

(302) Dobbs, K. D.; Dixon, D. A.; Komornicki, A. *J. Chem. Phys.* **1993**, *98*, 8852–8858.

(303) Jursic, B. S. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3467–3471.

(304) Aliagas, I.; Gronert, S. *J. Phys. Chem.* **1998**, *102*, 2609–2612.

(305) Bahri, M.; Jaïdane, N.; Ben Lakhdar, Z.; Flament, J. P. *J. Chim. Phys.* **1999**, *96*, 634–646.

(306) Skokov, S.; Wheeler, R. A. *Chem. Phys. Lett.* **1997**, *271*, 251–258.

(307) Garcia-Cruz, I.; Ruiz-Santoyo, M. E.; Alvarez-Idaboy, J. R.; Vivier-Bunge, A. *J. Comput. Chem.* **1999**, *20*, 845–856.

(308) Tsiouris, M.; Wheeler, M. D.; Lester, M. I. *Chem. Phys. Lett.* **1999**, *302*, 192–198.

(309) Masgrau, L.; González-Lafont, A.; Lluch, J. M. *J. Chem. Phys.* **2001**, *114*, 2154–2165.

(310) Espinosa-Garcia, J.; Corchado, J. C. *J. Chem. Phys.* **2000**, *112*, 5731–5739.

(311) Gierczak, T.; Talukdar, R. K.; Herndon, S. C.; Vaghjiani, G. L.; Ravishankara, A. R. *J. Phys. Chem.* **1997**, *101*, 3125–3134.

(312) Ruscic, B.; Berkowitz, J.; Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 114–121.

(313) Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847–9855.

(314) Tully, F. P.; Droege, A. T.; Koszykowski, M. L.; Melius, C. F. *J. Phys. Chem.* **1986**, *90*, 691–698.

(315) Droege, A. T.; Tully, F. P. *J. Phys. Chem.* **1987**, *91*, 1222–1225.

(316) Tully, F. P.; Goldsmith, J. E. M.; Droege, A. T. *J. Phys. Chem.* **1986**, *90*, 5932–5937.

(317) Hu, W.-P.; Rossi, I.; Corchado, J. C.; Truhlar, D. G. *J. Phys. Chem.* **1997**, *101*, 6911–6921.

(318) Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. *J. Phys. Chem.* **1997**, *101*, 8042–8048.

(319) Lobachev, V. L.; Rudakov, E. S. *Kinet. Catal.* **2000**, *41*, 186–195.

(320) Darnall, K. R.; Atkinson, R.; Pitts, J. N., Jr. *J. Phys. Chem.* **1978**, *82*, 1581–1584.

(321) Droege, A. T.; Tully, F. P. *J. Phys. Chem.* **1986**, *90*, 5937–5941.

(322) Talukdar, R. K.; Mellouki, A.; Gierczak, T.; Barone, S.; Chiang, S.-Y.; Ravishankara, A. R. *Int. J. Chem. Kinet.* **1994**, *26*, 973–990.

(323) Donahue, N. M.; Anderson, J. G.; Demerjian, K. L. *J. Phys. Chem.* **1998**, *102*, 3121–3126.

(324) Dóbé, S.; Turányi, T.; Iogansen, A. A.; Bérces, T. *Int. J. Chem. Kinet.* **1992**, *24*, 191–198.

(325) DeMore, W. B.; Bayes, K. D. *J. Phys. Chem.* **1999**, *103*, 2649–2654.

(326) Buda, F.; Ensing, B.; Gribnau, M. C. M.; Baerends, E. J. *Chem. Eur. J.* **2001**, *7*, 2775–2783.

(327) Gozzo, F. *J. Mol. Catal.* **2001**, *171*, 1–22.

(328) Walling, C. *Acc. Chem. Res.* **1998**, *31*, 155–157.

(329) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *Acc. Chem. Res.* **1998**, *31*, 159–162.

(330) Barton, D. H. R.; Csuhai, E.; Doller, D.; Ozbalik, N.; Senglet, N. *Tetrahedron Lett.* **1990**, *31*, 3097–3100.

(331) Yamazaki, I.; Piette, L. H. *J. Am. Chem. Soc.* **1991**, *113*, 7588–7593.

(332) Sawyer, D. T.; Kang, C.; Llobet, A.; Redman, C. *J. Am. Chem. Soc.* **1993**, *115*, 5817–5818.

(333) Sawyer, D. T.; Sobkowiak, A.; Matsushita, T. *Acc. Chem. Res.* **1996**, *29*, 409–416.

(334) Goldstein, S.; Meyerstein, D. *Acc. Chem. Res.* **1999**, *32*, 547–550.

(335) Roelfes, G.; Lubben, M.; Hage, R.; Que, L., Jr.; Feringa, B. L. *Chem. Eur. J.* **2000**, *6*, 2152–2159.

(336) Balavoine, G.; Barton, D. H. R.; Boivin, J.; Lecoupanec, P.; Lelandais, P. *New J. Chem.* **1989**, *13*, 691–700.

(337) Singh, B.; Long, J. R.; de Biani, F. F.; Gatteschi, D.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 7030–7047.

(338) Barton, D. H. R.; Boivin, J.; Gastiger, M.; Morzycki, J.; Hay-Motherwell, R. S.; Motherwell, W. B.; Ozbalik, N.; Schwartzentruber, K. M. *J. Chem. Soc., Perkin Trans. 1* **1986**, 947–955.

(339) Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504–512.

(340) Knight, C.; Perkins, M. J. *J. Chem. Soc., Chem. Commun.* **1991**, 925–927.

(341) Minisci, F.; Fontana, F. *Tetrahedron Lett.* **1994**, *35*, 1427–1430.

(342) Barton, D. H. R.; Hill, D. R. *Tetrahedron Lett.* **1994**, *35*, 1431–1434.

(343) Barton, D. H. R. *Synlett* **1997**, 229–230.

(344) Recupero, F.; Bravo, A.; Bjorsvik, H.-R.; Fontana, F.; Minisci, F.; Piredda, M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2399–2405.

(345) Barton, D. H. R.; Chabot, B. M.; Hu, B. *Tetrahedron* **1996**, *52*, 10301–10312.

(346) Bardin, C.; Barton, D. H. R.; Hu, B.; Rojas-Wahl, R.; Taylor, D. K. *Tetrahedron Lett.* **1994**, *35*, 5805–5808.

(347) Barton, D. H. R.; Chabot, B. M. *Tetrahedron* **1997**, *53*, 511–520.

(348) Barton, D. H. R.; Launay, F.; Le Gloahec, V. N.; Li, T. S.; Smith, F. *Tetrahedron Lett.* **1997**, *38*, 8491–8494.

(349) Barton, D. H. R.; Le Gloahec, V. N. *Tetrahedron Lett.* **1998**, *39*, 4413–4416.

(350) Barton, D. H. R.; Li, T. S.; Peralez, E. *Tetrahedron* **1998**, *54*, 15087–15096.

(351) Barton, D. H. R.; Salgueiro, M. C.; MacKinnon, J. *Tetrahedron* **1997**, *53*, 7417–7428.

(352) Barton, D. H. R.; Li, T. S. *Tetrahedron* **1998**, *54*, 1735–1744.

(353) Barton, D. H. R.; Chabot, B. M. *Tetrahedron* **1997**, *53*, 487–510.

(354) Marr, S. B.; Carvel, R. O.; Richens, D. T.; Lee, H.-J.; Lane, M.; Stavropoulos, P. *Inorg. Chem.* **2000**, *39*, 4630–4638.

(355) Kiani, S.; Tapper, A.; Staples, R. J.; Stavropoulos, P. *J. Am. Chem. Soc.* **2000**, *122*, 7503–7517.

(356) Stavropoulos, P.; Çelenligil-Çetin, R.; Tapper, A. E. *Acc. Chem. Res.* **2001**, *34*, 745–752.

(357) Kojima, T.; Leising, R. A.; Yan, S. P.; Que, L. J. *J. Am. Chem. Soc.* **1993**, *115*, 11328–11335.

(358) Newcomb, M.; Simakov, P. A. *Tetrahedron* **1998**, *39*, 965–966.

(359) MacFaul, P. A.; Ingold, K. U.; Wayner, D. D. M.; Que, L., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 10594–10598.

(360) Barton, D. H. R.; Csuhai, É.; Doller, D. *Tetrahedron Lett.* **1992**, *48*, 9195–9206.

(361) Shul′pin, G. B.; Guerreiro, M. C.; Schuchardt, U. *Tetrahedron* **1996**, *52*, 13051–13062.

(362) Süss-Fink, G.; Stanislas, S.; Shul′pin, G. B.; Nizova, G. V.; Stoeckli-Evans, H.; Neels, A.; Bobillier, C.; Claude, S. *J. Chem. Soc., Dalton Trans.* **1999**, 3169–3175.

(363) Shul′pin, G. B.; Kozlov, Y. N.; Nizova, G. V.; Süss-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1353–1371.

(364) Shul′pin, G. B.; Süss-Fink, G.; Smith, J. R. L. *Tetrahedron* **1999**, *55*, 5345–5358.

(365) Mizuno, N.; Nozaki, C.; Kiyoto, I.; Misono, M. *J. Am. Chem. Soc.* **1998**, *120*, 9267–9272.

(366) Fu, Y. J.; Lewis-Bevan, W.; Tyrrell, J. *J. Phys. Chem.* **1995**, *99*, 630–633.

(367) Lien, P.-Y.; You, R.-M.; Hu, W.-P. *J. Phys. Chem.* **2001**, *105*, 2391–2400.

(368) Schwartz, M.; Marshall, P.; Berry, R. J.; Ehlers, C. J.; Petersson, G. A. *J. Phys. Chem.* **1998**, *102*, 10074–10081.

(369) Jursic, B. S. *Chem. Phys. Lett.* **1996**, *256*, 603–608.

(370) Bottoni, A.; Poggi, G.; Emmi, S. S. *J. Mol. Struct. (THEOCHEM)* **1993**, *98*, 299–309.

(371) Korchowiec, J.; Kawahara, S.; Matsumura, K.; Uchimaru, T.; Sugie, M. *J. Phys. Chem.* **1999**, *103*, 3548–3553.

(372) Chandra, A. K.; Uchimaru, T.; Sugie, M. *J. Comput. Chem.* **2000**, *21*, 1305–1318.

(373) Sekusak, S.; Sabljic, A. *J. Comput. Chem.* **1997**, *18*, 1190–1199.

(374) Chandra, A. K.; Uchimaru, T. *J. Phys. Chem.* **1999**, *103*, 10874–10883.

(375) Louis, F.; Gonzalez, C. A.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem.* **2000**, *104*, 2931–2938.

(376) Sekusak, S.; Cory, M. G.; Bartlett, R. J.; Sabljic, A. *J. Phys. Chem.* **1999**, *103*, 11394–11405.

(377) Sekusak, S.; Sabljic, A. *Chem. Phys. Lett.* **1997**, *272*, 353–360.

(378) Yamada, T.; Fang, T. D.; Taylor, P. H.; Berry, R. J. *J. Phys. Chem.* **2000**, *104*, 5013–5022.

(379) Louis, F.; Gonzalez, C. A.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem.* **2001**, *105*, 1599–1604.

(380) Pardo, L.; Banfelder, J. R.; Osman, R. *J. Am. Chem. Soc.* **1992**, *114*, 2382–2390.

(381) Tsang, W. *J. Phys. Chem. Ref. Data* **1987**, *16*, 471–508.

(382) Hess, W. P.; Tully, F. P. *J. Phys. Chem.* **1989**, *93*, 1944–1947.

(383) Jodkowski, J. T.; Rayez, M.-T.; Rayez, J.-C.; Bérces, T.; Dóbé, S. *J. Phys. Chem.* **1999**, *103*, 3750–3765.

(384) Seki, Y.; Min, J. S.; Misono, M.; Mizuno, N. *J. Phys. Chem.* **2000**, *104*, 5940–5944.

(385) Nizova, G. V.; Süss-Fink, G.; Shul′pin, G. B. *Tetrahedron* **1997**, *53*, 3603–3614.

(386) Merkx, M.; Kopp, D. A.; Sazinsky, M. H.; Blazyk, J. L.; Müller, J.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2782–2807.

(387) Clyne, M. A. A.; Watson, R. T. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 2250–2259.

(388) Clyne, M. A. A.; Cruse, H. W. *J. Chem. Soc., Faraday Trans.* **1970**, *66*, 2227–2236.

(389) Francisco, J. S.; Su, Y. *Chem. Phys. Lett.* **1993**, *215*, 417–422.

(390) Louis, F.; Allison, T. C.; Gonzalez, C. A.; Sawerysyn, J.-P. *J. Phys. Chem.* **2001**, *105*, 4284–4289.

(391) Tsentalovich, Y. P.; Kulik, L. V.; Gritsan, N. P.; Yurkovskaya, A. V. *J. Phys. Chem.* **1998**, *102*, 7975–7980.

(392) Ogliaro, F.; Filatov, M.; Shaik, S. *Eur. J. Inorg. Chem.* **2000**, 2455–2458.

(393) Walling, C.; Kurkov, V. P. *J. Am. Chem. Soc.* **1967**, *89*, 4895–4901.

(394) Walling, C.; Mintz, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1515−1519.

(395) Paul, H.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520−4527.

(396) Wong, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 1235−1239.

(397) Weber, M.; Fischer, H. *J. Am. Chem. Soc.* **1999**, *121*, 7381−7388.

(398) Opeida, R. A.; Dmitric, A. F.; Zarechnaya, O. M. *Russ. Chem. Bull.* **2001**, *50*, 241−244.

(399) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106−5108.

(400) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208−211.

(401) Baban, J. A.; Goddard, J. P.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1269−1274.

(402) Dokolas, P.; Loffler, S. M.; Solomon, D. H. *Aust. J. Chem.* **1998**, *51*, 1113−1120.

(403) Dneprovskii, A. S.; Eliseenkov, E. V.; Kuznetsov, D. V. *Zh. Org. Khim.* **1994**, *30*, 232−235.

(404) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69−80.

(405) Freeman, P. K.; Ziebarth, T. D. *J. Org. Chem.* **1976**, *41*, 949−952.

(406) Reddy, D. S.; Maggini, M.; Tsanaktsidis, J.; Eaton, P. E. *Tetrahedron Lett.* **1990**, 805−806.

(407) Tanner, D. D.; Gidley, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 808−809.

(408) Choi, S.-Y.; Eaton, P. E.; Hollenberg, P. F.; Liu, K. E.; Lippard, S. J.; Newcomb, M.; Putt, D. A.; Upadhyaya, S. P.; Xiong, Y. S. *J. Am. Chem. Soc.* **1996**, *118*, 6547−6555.

(409) Karki, S. B.; Dinnocenzo, J. P.; Jones, J. P.; Korzekwa, K. R. *J. Am. Chem. Soc.* **1995**, *117*, 3657−3664.

(410) MacFaul, P. A.; Arends, I. W. C. E.; Ingold, K. U.; Wayner, D. D. M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 135−145.

(411) Barton, D. H. R.; Le Gloahec, V. N.; Patin, H. *New J. Chem.* **1998**, 565−568.

(412) Kim, J.; Harrison, R. G.; Kim, C.; Que, L., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 4373−4379.

(413) Leising, R. A.; Norman, R. E.; Que, L. J. *Inorg. Chem.* **1990**, *29*, 2553−2555.

(414) Nguyen, C.; Guajardo, R. J.; Mascharak, P. K. *Inorg. Chem.* **1996**, *35*, 6273−6281.

(415) Vincent, J.-M.; Béarnais-Barbry, S.; Pierre, C.; Verlhac, J.-B. *J. Chem. Soc., Dalton Trans.* **1999**, 1913−1914.

(416) Kim, J.; Kim, C.; Harrison, R. G.; Wilkinson, E. C.; Que, L., Jr. *J. Mol. Catal.* **1997**, *117*, 83−89.

(417) Arends, I. W. C. E.; Ingold, K. U.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 4710−4711.

(418) Ganeshpure, P. A.; Tembe, G. L.; Satish, S. *J. Mol. Catal.* **1996**, *113*, L423−L425.

(419) Ohta, T.; Tachiyama, T.; Yoshizawa, K.; Yamabe, T.; Uchida, T.; Kitagawa, T. *Inorg. Chem.* **2000**, *39*, 4358−4369.

(420) Launay, F.; Patin, H. *New J. Chem.* **1997**, *21*, 247−256.

(421) Kojima, T.; Matsuo, H.; Matsuda, Y. *Inorg. Chim. Acta* **2000**, *300−302*, 661−667.

(422) Chatterjee, D.; Mitra, A.; Mukherjee, S. *Polyhedron* **1999**, *18*, 2659−2663.

(423) Dell′Anna, M. M.; Mastrorilli, P.; Nobile, C. F. *J. Mol. Catal.* **1998**, *130*, 65−71.

(424) Shul′pin, G. B.; Süss-Fink, G.; Shul′pina, L. S. *J. Mol. Catal.* **2001**, *170*, 17−34.

(425) Chavez, F. A.; Nguyen, C. V.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1996**, *35*, 6282−6291.

(426) Chavez, F. A.; Rowland, J. M.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 9015−9027.

(427) Çelenligil-Çetin, R.; Staples, R. J.; Stavropoulos, P. *Inorg. Chem.* **2000**, *39*, 5838−5846.

(428) Costas, M.; Llobet, A. *J. Mol. Catal.* **1999**, *142*, 113−124.

(429) Fujiwara, M.; Xu, Q.; Souma, Y.; Kobayashi, T. *J. Mol. Catal.* **1999**, *142*, 77−84.

(430) Cramarossa, M. R.; Forti, L.; Fedotov, M. A.; Detusheva, L. G.; Likholobov, V. A.; Kuznetsova, L. I.; Semin, G. L.; Cavani, F.; Trifirò, F. *J. Mol. Catal.* **1997**, *127*, 85−94.

(431) Tateiwa, J.-i.; Horiuchi, H.; Uemura, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2013−2017.

(432) Ménage, S.; Vincent, J. M.; Lambeaux, C.; Chottard, G.; Grand, A.; Fontecave, M. *Inorg. Chem.* **1993**, *32*, 4766−4773.

(433) Minisci, F.; Fontana, F.; Zhao, L. H.; Banfi, S.; Quici, S. *Tetrahedron Lett.* **1994**, *35*, 8033−8036.

(434) Mekmouche, Y.; Duboc-Toia, C.; Ménage, S.; Lambeaux, C.; Fontecave, M. *J. Mol. Catal.* **2000**, *156*, 85−89.

(435) Leising, R. A.; Kim, J. H.; Pérez, M. A.; Que, L., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 9524−9530.

(436) Buchanan, R. M.; Chen, S.; Richardson, J. F.; Bressan, M.; Forti, L.; Morvillo, A.; Fish, R. H. *Inorg. Chem.* **1994**, *33*, 3208−3209.

(437) Balkus, K. J., Jr.; Eissa, M.; Levado, R. *J. Am. Chem. Soc.* **1995**, *117*, 10753−10754.

(438) Launay, F.; Roucoux, A.; Patin, H. *Tetrahedron Lett.* **1998**, *39*, 1353−1356.

(439) Hikichi, S.; Komatsuzaki, H.; Akita, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4699−4710.

(440) Muzart, J. *Chem. Rev.* **1992**, *92*, 113−140.

(441) Neimann, K.; Neumann, R.; Rabion, A.; Buchanan, R. M.; Fish, R. H. *Inorg. Chem.* **1999**, *38*, 3575−3850.

(442) Singh, B.; Long, J. R.; de Biani, F. F.; Gatteschi, D.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 7030−7047.

(443) Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F. *Tetrahedron Lett.* **1994**, *35*, 3759−3762.

(444) Perkins, M. J. *Chem. Soc. Rev.* **1996**, *25*, 229−236.

(445) Snelgrove, D. W.; MacFaul, P. A.; Ingold, K. U.; Wayner, D. D. M. *Tetrahedron Lett.* **1996**, *37*, 823−826.

(446) Barton, D. H. R.; Chavasiri, W. *Tetrahedron* **1994**, *50*, 19−30.

(447) Barton, D. H. R.; Bévière, S. D.; Chavasiri, W. *Tetrahedron* **1994**, *50*, 31−46.

(448) Barton, D. H. R.; Bévière, S. D.; Chavasiri, W.; Csuhai, E.; Doller, D.; Liu, W.-G. *J. Am. Chem. Soc.* **1992**, *114*, 2147−2156.

(449) Barton, D. H. R.; Chabot, B. M.; Delanghe, N. C.; Hu, B.; Le Gloahec, V. N.; Rojas Wahl, R. U. *Tetrahedron Lett.* **1995**, *36*, 7007−7010.

(450) Barton, D. H. R.; Le Gloahec, V. N.; Patin, H.; Launay, F. *New J. Chem.* **1998**, 559−563.

(451) Costas, M.; Chen, K.; Que, L., Jr. *Coord. Chem. Rev.* **2000**, *200−202*, 517−544.

(452) Giese, B.; Barbosa, F.; Stahelin, C.; Sauer, S.; Wettstein, P.; Wyss, C. *Pure Appl. Chem.* **2000**, *72*, 1623−1629.

(453) Giese, B.; Wettstein, P.; Stahelin, C.; Barbosa, F.; Neuburger, M.; Zehnder, M.; Wessig, P. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2586−2587.

(454) Barone, S. B.; Turnipseed, A. A.; Ravishankara, A. R. *J. Phys. Chem.* **1994**, *98*, 4602−4608.

(455) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466−470.

(456) Chenier, J. H. B.; Tong, S. B.; Howard, J. A. *Can. J. Chem.* **1978**, *56*, 3047−3053.

(457) Denisov, E. T.; Denisova, T. G. *Kinet. Catal.* **1993**, *34*, 883−889.

(458) Murahashi, S.-I.; Komiya, N.; Oda, Y.; Kuwabara, T.; Naota, T. *J. Org. Chem.* **2000**, *65*, 9186−9193.

(459) Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F.; Zhao, L. H. *Synlett* **1996**, 119−125.

(460) Das, T. N.; Dhanasekaran, T.; Alfassi, Z. B.; Neta, P. *J. Phys. Chem.* **1998**, *102*, 280−284.

(461) Kharasch, M. S.; Fono, A. *J. Org. Chem.* **1959**, *24*, 72−78.

(462) Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F.; Banfi, S.; Quici, S. *J. Am. Chem. Soc.* **1995**, *117*, 226−232.

(463) Bravo, A.; Bjorsvik, H.-R.; Fontana, F.; Minisci, F.; Serri, A. *J. Org. Chem.* **1996**, *61*, 9409−9416.

(464) Tokumaru, K.; Simamura, O. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1678−1683.

(465) Schneider, H. J.; Müller, W. *J. Org. Chem.* **1985**, *60*, 4609−4615.

(466) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2886−2893.

(467) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877−2885.

(468) Fossey, J.; Lefort, D.; Massoudi, M.; Nedelec, J.-Y.; Sorba, J. *Can. J. Chem.* **1985**, *63*, 678−680.

(469) Krasutsky, A. P.; Kuehl, C. J.; Zhdankin, V. V. *Synlett* **1995**, 1081−1082.

(470) Zhdankin, V. V.; Krasutsky, A. P.; Kuehl, C. J.; Simonsen, A. J.; Woodward, J. K.; Mismash, B.; Bolz, J. T. *J. Am. Chem. Soc.* **1996**, *118*, 5192−5197.

(471) Zhdankin, V. V.; McSherry, M.; Mismash, B.; Bolz, J. T.; Woodward, J. K.; Arbit, R. M.; Erickson, S. *Tetrahedron Lett.* **1997**, *38*, 21−24.

(472) Bravo, A.; Fontana, F.; Minisci, F.; Serri, A. *Chem. Commun.* **1996**, 1843−1844.

(473) Smith, J. R. L.; Shul′pin, G. B. *Tetrahedron Lett.* **1998**, *39*, 4909−4912.

(474) Deno, N. C.; Messer, L. A. *J. Chem. Soc., Chem. Commun.* **1976**, 1051.

(475) Moody, C. J.; O'Connell, J. L. *Chem. Commun.* **2000**, 1311−1312.

(476) Layng, T. E.; Sourkop, R. *Ind. Eng. Chem.* **1928**, *20*, 1052.

(477) Takemoto, T.; Tabata, K.; Teng, Y. H.; Nakayama, A.; Suzuki, E. *Appl. Catal.* **2001**, *205*, 51−59.

(478) Yamaguchi, Y.; Teng, Y.; Shimomura, S.; Tabata, K.; Suzuki, E. *J. Phys. Chem.* **1999**, *103*, 8272−8278.

(479) Tabata, K.; Teng, Y. H.; Yamaguchi, Y.; Sakurai, H.; Suzuki, E. *J. Phys. Chem.* **2000**, *104*, 2648−2654.

(480) Chan, W.-T.; Heck, S. M.; Pritchard, H. O. *Phys. Chem. Chem. Phys.* **2001**, *3*, 56−62.

(481) Teng, Y. H.; Yamaguchi, Y.; Takemoto, T.; Tabata, K.; Suzuki, E. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3429−3433.

(482) Mori, T.; Suzuki, H. *Synlett* **1995**, 383−392.

(483) Martínez, E.; Cabañas, B.; Aranda, A.; Martín, P.; Notario, A.; Salgado, S. *J. Phys. Chem.* **1999**, *103*, 5321−5327.

(484) Stanton, J. F.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 5554−5559.

(485) Atkinson, R. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459−507.

(486) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215−290.

(487) Aschmann, S. M.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 2311−2316.

(488) Glass, R. W.; Martin, T. W. *J. Am. Chem. Soc.* **1970**, *92*, 5084−5093.
(489) Baciocchi, E.; Del Giacco, T.; Rol, C.; Sebastiani, G. V. *Tetrahedron Lett.* **1985**, 541−544.
(490) Suzuki, H.; Nonoyama, N. *Chem. Commun.* **1996**, 1783−1784.
(491) Suzuki, H.; Nonoyama, N. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2965−2971.
(492) Fokin, A. A.; Peleshanko, S. A.; Gunchenko, P. A.; Gusev, D. V.; Schreiner, P. R. *Eur. J. Org. Chem.* **2000**, 3357−3362.
(493) Ishikawa, S.; Nojima, T.; Sawaki, Y. *J. Chem. Soc., Perkin Trans. 2* **1996**, 127−132.
(494) Bottle, S. E.; Chand, U.; Micallef, A. S. *Chem. Lett.* **1997**, 857−858.
(495) Ishii, Y.; Iwahama, T.; Sakaguchi, S.; Nakayama, K.; Nishiyama, Y. *J. Org. Chem.* **1996**, *61*, 4520−4526.
(496) Ishii, Y.; Nakayama, K.; Takeno, M.; Sakaguchi, S.; Iwahama, T.; Nishiyama, Y. *J. Org. Chem.* **1995**, *60*, 3934−3935.
(497) Yoshino, Y.; Hayashi, Y.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1997**, *62*, 6810−6813.
(498) Sakaguchi, S.; Kato, S.; Iwahama, T.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1237−1240.
(499) Kato, S.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1998**, *63*, 222−223.
(500) Ishii, Y.; Kato, S.; Iwahama, T.; Sakaguchi, S. *Tetrahedron Lett.* **1996**, *37*, 4993−4996.
(501) Sakaguchi, S.; Nishiwaki, Y.; Kitamura, T.; Ishii, Y. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 222−224.
(502) Isozaki, S.; Nishiwaki, Y.; Sakaguchi, S.; Ishii, Y. *Chem. Commun.* **2001**, 1352−1353.
(503) Mella, M.; Freccero, M.; Albini, A. *Tetrahedron* **1996**, *52*, 5549−5562.
(504) Cardarelli, A. M.; Fagnoni, M.; Mella, M.; Albini, A. *J. Org. Chem.* **2001**, *66*, 7320−7327.
(505) Gilbert, B. C.; Smith, J. R. L.; Taylor, P.; Ward, S.; Whitwood, A. C. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1631−1637.
(506) Lin, M. R.; Sen, A. M. *J. Chem. Soc., Chem. Commun.* **1992**, 892−893.
(507) Padmaja, S.; Alfassi, Z. B.; Neta, P.; Huie, R. E. *Int. J. Chem. Kinet.* **1993**, *25*, 193−198.
(508) Sen, A.; Benvenuto, M. A.; Lin, M. R.; Hutson, A. C.; Basickes, N. *J. Am. Chem. Soc.* **1994**, *116*, 998−1003.
(509) Leroy, G.; Sana, M.; Tinant, A. *Can. J. Chem.* **1985**, *63*, 1447−1456.
(510) Basch, H.; Hoz, S. *J. Phys. Chem.* **1997**, *101*, 4416−4431.
(511) Yu, Y.-X.; Li, S.-M.; Xu, Z.-F.; Li, Z.-S.; Sun, C.-C. *Chem. Phys. Lett.* **1998**, *296*, 131−136.
(512) Mebel, A. M.; Moskaleva, L. V.; Lin, M. C. *J. Mol. Struct. (THEOCHEM)* **1999**, *461*−*462*, 223−238.
(513) Mebel, A. M.; Lin, M. C. *J. Phys. Chem.* **1999**, *103*, 2088−2096.
(514) Demissy, M.; Lesclaux, R. *J. Am. Chem. Soc.* **1985**, *102*, 2897−2902.
(515) Yu, Y.-X.; Li, S.-M.; Xu, Z.-F.; Li, Z.-S.; Sun, C.-C. *Chem. Phys. Lett.* **1999**, *302*, 281−287.
(516) Ehbrecht, J.; Hack, W.; Rouveirolles, P.; Wagner, H. G. *Ber. Bun. Phys. Chem.* **1987**, *91*, 700−708.
(517) Hack, W.; Kurzke, H.; Rouveirolles, P.; Wagner, H. G. *Ber. Bun. Phys. Chem.* **1986**, *90*, 1210−1219.
(518) Hennig, G.; Wagner, H. G. *Ber. Bun. Phys. Chem.* **1995**, *99*, 863−869.
(519) Krajnik, P.; Michos, D.; Crabtree, R. H. *New J. Chem.* **1993**, *17*, 805−813.
(520) Traynham, J. G.; Lee, Y.-S. *J. Am. Chem. Soc.* **1974**, *96*, 3590−3594.
(521) Tabushi, I.; Yoshida, Z.; Aoyama, Y.; Hamuro, J.; Kojo, S. *J. Am. Chem. Soc.* **1972**, *94*, 1177−1183.
(522) Skell, P. S.; Seshadri, S. *J. Org. Chem.* **1984**, *49*, 1650−1653.
(523) Tlumak, R. L.; Day, J. C.; Slanga, J. P.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7257−7267.
(524) Merényi, G.; Lind, J.; Eberson, L. *Acta Chem. Scand.* **1998**, *52*, 62−66.
(525) Johnson, R. A.; Greene, F. D. *J. Org. Chem.* **1975**, *40*, 2192−2196.
(526) Smith, G. W.; Williams, H. D. *J. Org. Chem.* **1961**, *26*, 2207−2212.
(527) Deno, N. C. In *Methods in free-radical chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1975; p 143.
(528) Bernardi, R.; Galli, R.; Minisci, F. *J. Chem. Soc.* **1968**, 324−325.
(529) Minisci, F.; Galli, R.; Galli, A.; Bernardi, R. *Tetrahedron Lett.* **1967**, 2207−2209.
(530) Wünsch, E.; Lluch, J. M.; Oliva, A.; Bertrán, J. *J. Chem. Soc., Perkin Trans. 2* **1987**, 211−213.
(531) Fan, L.; Ziegler, T. *J. Am. Chem. Soc.* **1992**, *114*, 10890−10897.
(532) Jursic, B. S. *Chem. Phys. Lett.* **1995**, *244*, 263−268.
(533) *CRC Handbook of Bimolecular and Termolecular Gas Reactions*; CRC Press: Boca Raton, 1981.
(534) Chandra, A. K.; Padma Malar, E. J.; Sen Gupta, D. *Int. J. Quantum Chem.* **1992**, *41*, 371−379.
(535) Bu, Y.; Ding, Y.; Deng, C. *J. Mol. Struct. (THEOCHEM)* **1997**, *417*, 69−80.
(536) Creak, G. A.; Dainton, F. S.; Ivin, K. J. *J. Chem. Soc., Faraday Trans.* **1962**, 326.
(537) Canadell, E.; Olivella, S.; Poblet, J. M. *J. Phys. Chem.* **1984**, *88*, 3545−3549.
(538) Kopinke, F.-D.; Remmler, M.; Mensing, H.; Hugo, P. *J. Phys. Chem.* **1994**, *98*, 1171−1175 and references therein.
(539) Hendry, D. G.; Mill, T.; Piszkiewicz, L.; Howard, J. A.; Eigenmann, H. K. *J. Phys. Chem. Ref. Data* **1974**, *3*, 937−978.
(540) Olleta, A. C.; Taccone, R. A. *J. Mol. Struct. (THEOCHEM)* **2000**, *507*, 25−38.
(541) Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511−527.
(542) Pritchard, G. O.; Bryant, J. T.; Thommarson, R. L. *J. Phys. Chem.* **1965**, *69*, 664−665.
(543) Hunter, W. H.; Edgar, D. E. *J. Am. Chem. Soc.* **1932**, *54*, 2025.
(544) Gershuni, S.; Itzhak, N.; Rabani, J. *Langmuir* **1999**, *15*, 1141−1146.
(545) Huyser, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 391−393.
(546) Smirnov, V. V.; Zelikman, V. M.; Beletskaya, I. P.; Levitskii, M. M.; Kazankova, M. A. *Mendeleev Commun.* **2000**, 175−176.
(547) Davis, R.; Durrant, J. L. A.; Rowland, C. C. *J. Organomet. Chem.* **1986**, *316*, 147−162.
(548) Smirnov, V. V.; Golubeva, E. N.; Zagorskaya, O. A.; Nevskaya, S. M.; Levitskii, M. M.; Zufman, V. Y. *Kinet. Catal.* **2000**, *41*, 399−401.
(549) Rogers, E. E.; Abramowitz, S.; Jacox, M. E.; Milligan, D. E. *J. Chem. Phys.* **1970**, *52*, 2198−2204.
(550) Hawari, J. A.; Davis, S.; Engel, P. S.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 4721−4724.
(551) Matheson, I.; Tedder, J.; Sidebottom, H. *Int. J. Chem. Kinet.* **1982**, *14*, 1033−1045.
(552) Matheson, I.; Tedder, J.; Sidebottom, H. *Int. J. Chem. Kinet.* **1983**, *15*, 904−913.
(553) Jursic, B. S. *J. Mol. Struct. (THEOCHEM)* **1996**, *365*, 75−80.
(554) Tanner, D. D.; Arhart, R. J.; Blackburn, E. V.; Das, N. C.; Wada, N. *J. Am. Chem. Soc.* **1974**, *96*, 829−834.
(555) Fell, B.; Kung, L.-H. *Chem. Ber.* **1965**, *98*, 2871−2886.
(556) Tabushi, I.; Aoyama, Y.; Kojo, S.; Hamuro, J.; Yoshida, Z.-i. *J. Am. Chem. Soc.* **1972**, *94*, 1177−1183.
(557) Perkins, R. R.; Pincock, R. E. *Can. J. Chem.* **1978**, *56*, 1269−1272.
(558) Vedernikov, A. N.; Sayakhov, M. D.; Zazybin, A. G.; Solomonov, B. N. *Zhurn. Org. Khim.* **1998**, *34*, 862−865.
(559) Sawyer, D. T.; Roberts, J. L. *Acc. Chem. Res.* **1988**, *21*, 469−476.
(560) Andrieux, C. P.; Savéant, J.-M.; Tardy, C. *J. Am. Chem. Soc.* **1998**, *120*, 4167−4175.
(561) Schreiner, P. R.; Lauenstein, O.; Kolomitsyn, I. V.; Nadi, S.; Fokin, A. A. *Angew. Chem.* **1998**, *110*, 1993−1995.
(562) Lauenstein, O.; Fokin, A. A.; Schreiner, P. R. *Org. Lett.* **2000**, 2201−2204.
(563) (a) Schreiner, P. R.; Lauenstein, O.; Butova, E. D.; Fokin, A. A. *Angew. Chem.* **1999**, *111*, 2956−2958. (b) Schreiner, P. R.; Lauenstein, O.; Butova, E. D.; Gunchenko, P. A.; Kolomitsin, I. V.; Wittkopp, A.; Feder, G.; Fokin, A. A. *Chem. Eur. J.* **2001**, *7*, 4996−5003.
(564) Camaioni, D. M.; Bays, J. T.; Shaw, W. J.; Linehan, J. C.; Birnbaum, J. C. *J. Org. Chem.* **2001**, *66*, 789−795.
(565) Dolbier, W. R., Jr. *Chem. Rev.* **1996**, *96*, 1557−1584.
(566) Bartberger, M. D.; Dolbier, W. R., Jr.; Lusztyk, J.; Ingold, K. U. *Tetrahedron* **1997**, *53*, 9857−9880.
(567) Hogan, T.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 2642−2646.
(568) Shtarev, A. B.; Tian, F.; Dolbier, W. R., Jr.; Smart, B. E. *J. Am. Chem. Soc.* **1999**, *121*, 7335−7341.
(569) Liguori, L.; Bjørsvik, H.-R.; Bravo, A.; Fontana, F.; Minisci, F. *Chem. Commun.* **1997**, 1501−1502.
(570) Minisci, F.; Fontana, F.; Recupero, F.; Bravo, A.; Pagano, E.; Rinaldi, C.; di Luca, M.; Grossi, F.; Bjørsvik, H.-R. *J. Am. Chem. Soc.* **1999**, *121*, 7760−7765.
(571) Tumanskii, B. L.; Shaposhnikova, E. N.; Avetisyan, E. A.; Sterlin, R. S. *J. Fluorine Chem.* **1999**, *96*, 47−50.
(572) Levy, L. A. *J. Chem. Soc., Chem. Commun.* **1978**, 574−575.
(573) Atakan, B.; Wolfrum, J. *Chem. Phys. Lett.* **1991**, *186*, 547−552.
(574) Ceursters, B.; Nguyen, H. M. T.; Peeters, J.; Nguyen, M. T. *Chem. Phys. Lett.* **2000**, *329*, 412−420.
(575) Kjær, N. T.; Lund, H. *Electrochim. Acta* **1997**, *42*, 2041−2047.
(576) Tokmakov, I. V.; Park, J.; Gheyas, S.; Lin, M. C. *J. Phys. Chem.* **1999**, *103*, 3636−3645.
(577) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609−3614.
(578) Rüchardt, C.; Gerst, M.; Ebenhoch, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1407−1430.
(579) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847−2853.
(580) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187−1201.

(581) Curci, R.; D'Accolti, L.; Fiorentino, M.; Fusco, C.; Adam, W.; Gonzalez-Nunez, M. E.; Mello, R. *Tetrahedron Lett.* **1992**, *33*, 4225−4228.
(582) Teager, D. S.; Murray, R. K., Jr. *J. Org. Chem.* **1993**, *58*, 5548−5550.
(583) Mello, R.; Cassidei, L.; Fiorentino, M.; Fusco, C.; Curci, R. *Tetrahedron Lett.* **1990**, *31*, 3067−3070.
(584) Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* **1989**, *111*, 6749−6757.
(585) desMarteau, D. D.; Donadelli, A.; Montanari, V.; Petrov, V. A.; Resnati, G. *J. Am. Chem. Soc.* **1993**, *115*, 4897−4898.
(586) Yang, D.; Wong, M.-K.; Wang, X.-C.; Tang, Y.-C. *J. Am. Chem. Soc.* **1998**, *120*, 6611−6612.
(587) Murray, R. W.; Jeyaraman, R.; Mohan, L. *J. Am. Chem. Soc.* **1986**, *108*, 2470−2472.
(588) Sorochinsky, A. E.; Petrenko, A. A.; Soloshonok, V. A.; Resnati, G. *Tetrahedron* **1997**, *53*, 5995−6000.
(589) Fusco, C.; Fiorentino, M.; Dinoi, A.; Curci, R. *J. Org. Chem.* **1996**, *61*, 8681−8684.
(590) Dehmlow, E. V.; Heiligenstädt, N. *Tetrahedron Lett.* **1996**, *37*, 5363−5364.
(591) Adam, W.; Curci, R.; D'Accolti, L.; Dinoi, A.; Fusco, C.; Gasparrini, F.; Kluge, R.; Paredes, R.; Schulz, M.; Smerz, A. K.; Veloza, L. A.; Weinkötz, S.; Winde, R. *Chem. Eur. J.* **1997**, *3*, 105−109.
(592) Adam, W.; Asensio, G.; Curci, R.; Gonzalez-Nuñez, M. E.; Mello, R. *J. Org. Chem.* **1992**, *57*, 953−955.
(593) Bravo, A.; Fontana, F.; Fronza, G.; Minisci, F.; Zhao, L. H. *J. Org. Chem.* **1998**, *63*, 254−263.
(594) Curci, R.; Dinoi, A.; Fusco, C.; Lillo, M. A. *Tetrahedron Lett.* **1996**, *37*, 249−252.
(595) Kabal'nova, N. N.; Khursan, S. L.; Shereshovets, V. V.; Tolstikov, G. A. *Kinet. Catal.* **1999**, *40*, 207−216.
(596) Bravo, A.; Fontana, F.; Fronza, G.; Mele, A.; Minisci, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1573−1574.
(597) Khusnullina, D. R.; Kazakov, D. V.; Kabal'nova, N. N.; Khursan, S. L.; Shereshovets, V. V. *Kinet. Catal.* **1998**, *39*, 4−7.
(598) Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* **1995**, *67*, 811−822.
(599) Asensio, G.; Mello, R.; Gonzalez-Nuñez, M. E.; Boix, C.; Royo, J. *Tetrahedron Lett.* **1997**, *38*, 2373−2376.
(600) Murray, R. W.; Pillay, M. K. *Tetrahedron Lett.* **1988**, *29*, 15−18.
(601) Murray, R. W.; Gu, H. *J. Org. Chem.* **1995**, *60*, 5673−5677.
(602) Minisci, F.; Zhao, L. H.; Fontana, F.; Bravo, A. *Tetrahedron Lett.* **1995**, *36*, 1697−1700.
(603) Minisci, F.; Zhao, L. H.; Fontana, F.; Bravo, A. *Tetrahedron Lett.* **1995**, *36*, 1895−1898.
(604) Murray, R. W.; Pillay, M. K.; Je-Yaraman, R. *J. Org. Chem.* **1988**, *53*, 3007−3011.
(605) Simakov, P. A.; Choi, S.-Y.; Newcomb, M. *Tetrahedron Lett.* **1998**, *39*, 8187−8190.
(606) Vanni, R.; Garden, S. J.; Banks, J. T.; Ingold, K. U. *Tetrahedron Lett.* **1995**, *36*, 7999−8002.
(607) Gräfenstein, J.; Cremer, D. *Chem. Phys. Lett.* **2000**, *316*, 569−577.
(608) Kraka, E.; Konkoli, Z.; Cremer, D.; Fowler, J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1996**, *118*, 10595−10608.
(609) Anglada, J. M.; Bofill, J. M.; Olivella, S.; Solé, A. *J. Phys. Chem.* **1998**, *102*, 3398−3406.
(610) Bach, R. D.; Andres, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1992**, *114*, 7207−7217.
(611) Du, X. H.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 6480−6483.
(612) Glukhovtsev, M. N.; Canepa, C.; Bach, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 10528−10533.
(613) Shustov, G. V.; Rauk, A. *J. Org. Chem.* **1998**, *63*, 5413−5422.
(614) Shaik, S.; Filatov, M.; Schröder, D.; Schwarz, H. *Chem. Eur. J.* **1998**, *4*, 193−199.
(615) Cremer, D.; Kraka, E.; Szalay, P. G. *Chem. Phys. Lett.* **1998**, *292*, 97−109.
(616) Freccero, M.; Gandolfi, R.; Sarzi-Amadè, M.; Rastelli, A. *Tetrahedron Lett.* **2001**, *42*, 2739−2742.
(617) Fokin, A. A.; Tkachenko, B. A.; Korshunov, O. I.; Gunchenko, P. A.; Schreiner, P. R. *J. Am. Chem. Soc.* **2001**, *123*, 11248−11252.
(618) Kazakov, D. V.; Barzilova, A. B.; Kazakov, V. P. *Chem. Commun.* **2001**, 191−192.
(619) Curci, R.; D'Accolti, L.; Fusco, C. *Tetrahedron Lett.* **2001**, *42*, 7087−7090.
(620) Shustov, G. V.; Spinney, R.; Rauk, A. *J. Am. Chem. Soc.* **2000**, *122*, 1191−1199.
(621) Richeson, C. E.; Mulder, P.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1998**, *120*, 7211−7219.
(622) Rudakov, E. S.; Lobachev, V. L.; Geletii, Y. V.; Balavoine, G. G. *Zh. Org. Khim.* **1996**, *32*, 522−528.
(623) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441−450.
(624) Lee, D. G.; Chen, T. *J. Am. Chem. Soc.* **1993**, *115*, 11231−11236.
(625) Étard, A.; Moissan, H. M. *C. R. Hebd. Seances Acad. Sci.* **1877**, *84*, 127.
(626) Suggs, J. W.; Ytuarte, L. *Tetrahedron Lett.* **1986**, *27*, 437−440.
(627) Sulima, L. V.; Gragerov, I. P. *Zhurn. Obsh. Khim.* **1959**, *29*, 3825−3831.
(628) Cristol, S. J.; Roberts, A. A.; McEntee, T. E. *J. Org. Chem.* **1974**, *39*, 829−831.
(629) Israel, R. J.; Murray, R. K. J. *J. Org. Chem.* **1983**, *48*, 4701−4705.
(630) Bingham, R. C.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 1198−1202.
(631) Rentea, C. N.; Rentea, M.; Necsoiu, I.; Nenitzescu, C. D. *Tetrahedron* **1968**, *24*, 4667−4676.
(632) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 3287−3294.
(633) Limberg, C. *Chem. Eur. J.* **2000**, *6*, 2083−2089.
(634) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 1855−1868.
(635) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7139−7156.
(636) Wang, K.; Mayer, J. M. *J. Org. Chem.* **1997**, *62*, 4248−4252.
(637) Wiberg, K. B.; Eisenthal, R. *Tetrahedron* **1964**, *20*, 1151−1161.
(638) Wistuba, T.; Limberg, C.; Kircher, P. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3037−3039.
(639) Bakac, A. *J. Am. Chem. Soc.* **2000**, *122*, 1092−1097.
(640) Fokin, A. A.; Gunchenko, P. A.; Tkachenko, B. A.; Butova, E. D.; Yurchenko, A. G. *Tetrahedron Lett.* **1997**, *38*, 639−642.
(641) Pestovsky, O.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 13422−13428.
(642) Brauman, J. I.; Pandell, A. J. *J. Am. Chem. Soc.* **1970**, *92*, 329−335.
(643) Deng, L. Q.; Ziegler, T. *Organometallics* **1996**, *15*, 3011−3021.
(644) Strassner, T.; Houk, K. N. *J. Am. Chem. Soc.* **2000**, *122*, 7821−7822.
(645) Stewart, R.; Spitzer, U. A. *Can. J. Chem.* **1978**, *56*, 1273−1279.
(646) Gardner, K. A.; Kuehnert, L. L.; Mayer, J. M. *Inorg. Chem.* **1997**, *36*, 2069−2078.
(647) Tenaglia, A.; Terranova, E.; Waegell, B. *J. Chem. Soc., Chem. Commun.* **1990**, 1344−1345.
(648) Tenaglia, A.; Terranova, E.; Waegell, B. *J. Org. Chem.* **1992**, *57*, 5523−5528.
(649) Lau, T.-C.; Mak, C.-K. *J. Chem. Soc., Chem. Commun.* **1993**, 766−767.
(650) Delaude, L.; Laszlo, P. *J. Org. Chem.* **1996**, *61*, 6360−6370.
(651) Bakke, J. M.; Bethell, D. *Acta Chem. Scand.* **1992**, *46*, 644−649.
(652) Bakke, J. M.; Brænden, J. E. *Acta Chem. Scand.* **1991**, *45*, 418−423.
(653) Ho, C. M.; Lau, T.-C. *New J. Chem.* **2000**, *24*, 587−590.
(654) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120−9132.
(655) Au, S.-M.; Huang, J.-S.; Che, C.-M.; Yu, W.-Y. *J. Org. Chem.* **2000**, *65*, 7858−7864.
(656) Nägeli, I.; Baud, C.; Bernardinelli, G.; Jacquier, Y.; Moran, M.; Müller, P. *Helv. Chim. Acta* **1997**, *80*, 1087−1105.
(657) Bakke, J. M.; Frøhaug, A. E. *Acta Chem. Scand.* **1994**, *48*, 160−164.
(658) Murahashi, S.-I.; Oda, Y.; Komiya, N.; Naota, T. *Tetrahedron Lett.* **1994**, *35*, 7953−7956.
(659) Komiya, N.; Noji, S.; Murahashi, S.-I. *Chem. Commun.* **2001**, 65−66.
(660) Kojima, T. *Chem. Lett.* **1996**, 121−122.
(661) Jitsukawa, K.; Oka, Y.; Einaga, H.; Masuda, H. *Tetrahedron Lett.* **2001**, *42*, 3467−3469.
(662) Ortiz de Montellano, P. R. *Acc. Chem. Res.* **1987**, *20*, 289−294.
(663) Davydov, R.; Makris, T. M.; Kofman, V.; Werst, D. E.; Sligar, S. G.; Hoffman, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 1403−1415.
(664) Hjelmeland, L. M.; Loew, G. H. *J. Am. Chem. Soc.* **1977**, *90*, 3514−3515.
(665) Chen, K.; Que, L., Jr. *Chem. Commun.* **1999**, 1375−1376.
(666) Ohno, T.; Suzuki, N.; Dokoh, T.; Urano, Y.; Kikuchi, K.; Hirobe, M.; Higuchi, T.; Nagano, T. *J. Inorg. Biochem.* **2000**, *82*, 123−125.
(667) Yoshizawa, K.; Shiota, Y.; Kagawa, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2669−2673.
(668) Nam, W.; Kim, I.; Kim, Y.; Kim, C. *Chem. Commun.* **2001**, 1262−1263.
(669) Guo, C.-C.; Song, J.-X.; Chen, X.-B.; Jiang, G.-F. *J. Mol. Catal.* **2000**, *157*, 31−40.
(670) Chen, K.; Que, L. *J. Am. Chem. Soc.* **2001**, *123*, 6327−6337.
(671) Harris, D. L.; Loew, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 8941−8948.
(672) Ortiz de Montellano, P. R. *Acc. Chem. Res.* **1998**, *31*, 543−549.
(673) Ho, R. Y. N.; Roelfes, G.; Hermant, R.; Hage, R.; Feringa, B. L.; Que, L. *Chem. Commun.* **1999**, 2161−2162.
(674) Hayano, M. In *Oxygenases*; Hayaishi, O., Ed.; Academic Press: New York, 1986; pp 181−240.
(675) Newcomb, M.; Toy, P. H. *Acc. Chem. Res.* **2000**, *33*, 449−455.
(676) Newcomb, M.; Le Tadic-Biadatti, M. H.; Chestney, D. L.; Roberts, E. S.; Hollenberg, P. F. *J. Am. Chem. Soc.* **1995**, *117*, 12085−12091.

(677) Ortiz de Montellano, P. R.; Stearns, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 3415–3420.
(678) Groves, J. T. *J. Chem. Educ.* **1985**, *62*, 928–931.
(679) Groves, J. T.; McClusky, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 859–861.
(680) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032–1033.
(681) Sono, M.; Roach, M. P.; Coulter, E. D.; Dawson, J. H. *Chem. Rev.* **1996**, *96*, 2841–2887.
(682) Collman, J. P.; Chien, A. S.; Eberspacher, T. A.; Brauman, J. I. *J. Am. Chem. Soc.* **2000**, *122*, 11098–11100.
(683) Jones, J. P.; Trager, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 2171–2173.
(684) Atkins, W. M.; Sligar, S. G. *J. Am. Chem. Soc.* **1987**, *109*, 3754–3760.
(685) Sorokin, A.; Robert, A.; Meunier, B. *J. Am. Chem. Soc.* **1993**, *115*, 7293–7299.
(686) Sorokin, A.; Khenkin, A. M. *J. Chem. Soc., Chem. Commun.* **1990**, 45–46.
(687) Lim, M. H.; Lee, Y. J.; Goh, Y. M.; Nam, W.; Kim, C. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 707–713.
(688) Manchester, J. I.; Dinnocenzo, J. P.; Higgins, L.; Jones, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 5069–5070.
(689) Newcomb, M.; Le Tadic, M.-H.; Putt, D. A.; Hollenberg, P. F. *J. Am. Chem. Soc.* **1995**, *117*, 3312–3313.
(690) Newcomb, M.; Shen, R.; Choi, S.-Y.; Toy, P. H.; Hollenberg, P. F.; Vaz, A. D. N.; Coon, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 2677–2686.
(691) Collman, J. P.; Chien, A. S.; Eberspacher, T. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1998**, *120*, 425–426.
(692) Toy, P. H.; Newcomb, M.; Hollenberg, P. F. *J. Am. Chem. Soc.* **1998**, *120*, 7719–7729.
(693) Filatov, M.; Harris, C. B.; Shaik, S. *J. Chem. Soc., Perkin Trans. 2* **1999**, 399–410.
(694) de Visser, S. P.; Ogliaro, F.; Shaik, S. *J. Inorg. Biochem.* **2001**, *86*, 198.
(695) Cohen, S.; Ogliaro, F.; de Visser, S. P.; Kaneti, J.; Shaik, S. *J. Inorg. Biochem.* **2001**, *86*, 183.
(696) Ogliaro, F.; Harris, N.; Cohen, S.; Filatov, M.; de Visser, S. P.; Shaik, S. *J. Am. Chem. Soc.* **2000**, *122*, 8977–8989.
(697) Yoshizawa, K.; Kagawa, Y.; Shiota, Y. *J. Phys. Chem.* **2000**, *104*, 12365–12370.
(698) Hata, M.; Hirano, Y.; Hoshino, T.; Tsuda, M. *J. Am. Chem. Soc.* **2001**, *123*, 6410–6416.
(699) Yoshizawa, K.; Kamachi, T.; Shiota, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9806–9816.
(700) Ogliaro, F.; de Visser, S. P.; Shaik, S. *J. Inorg. Biochem.* **2001**, *86*, 363.
(701) Nam, W.; Lim, M. H.; Moon, S. K.; Kim, C. *J. Am. Chem. Soc.* **2000**, *122*, 10805–10809.
(702) Nam, W. *J. Inorg. Biochem.* **2001**, *86*, 80.
(703) Toy, P. H.; Newcomb, M.; Coon, M. J.; Vaz, A. D. N. *J. Am. Chem. Soc.* **1998**, *120*, 9718–9719.
(704) Stearns, R. A.; Ortiz de Montellano, P. R. *J. Am. Chem. Soc.* **1985**, *107*, 4081–4082.
(705) Sato, H.; Guengerich, F. P. *J. Am. Chem. Soc.* **2000**, *122*, 8099–8100.
(706) Goto, Y.; Watanabe, Y.; Fukuzumi, S.; Jones, J. P.; Dinnocenzo, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 10762–10763.
(707) MacDonald, T. L.; Gutheim, W. G.; Martin, R. B.; Guengerich, F. P. *Biochemistry* **1989**, *28*, 2071–2077.
(708) Higgins, L.; Bennett, G. A.; Shimoji, M.; Jones, J. P. *Biochemistry* **1998**, *37*, 7039–7046.
(709) Adam, W.; Lukacs, Z.; Harmsen, D.; Saha-Möller, C. R.; Schreier, P. *J. Org. Chem.* **2000**, *65*, 878–882.
(710) Lipscomb, J. D.; Que, L. *J. Biol. Inorg. Chem.* **1998**, *3*, 331–336.
(711) Rosenzweig, A. C.; Lippard, S. J. *Acc. Chem. Res.* **1994**, *27*, 229–236.
(712) Brazeau, B. J.; Lipscomb, J. D. Enzyme-catalyzed electron and radical transfer. In *Subcellular Biochemistry*; Holzenburg, A., Scrutton, N. S., Eds.; Kluwer Academic/Plenum Publishers: New York, Boston, Dordrecht, London, Moscow, 2000; Vol. 35, pp 233–277.
(713) Whittington, D. A.; Lippard, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 827–838.
(714) Wallar, B. J.; Lipscomb, J. D. *Chem. Rev.* **1996**, *96*, 2625–2657.
(715) Chang, S.-L.; Wallar, B. J.; Lipscomb, J. D.; Mayo, K. H. *Biochemistry* **1999**, *38*, 5799–5812.
(716) Rosenzweig, A. C.; Nordlund, P.; Takahara, P. M.; Frederick, C. A.; Lippard, S. J. *Chem. Biol.* **1995**, *2*, 409–418.
(717) Que, L.; Dong, Y. H. *Acc. Chem. Res.* **1996**, *29*, 190–196.
(718) Yoshizawa, K.; Yokomichi, Y.; Shiota, Y.; Ohta, T.; Yamabe, T. *Chem. Lett.* **1997**, 587–588.
(719) Yoshizawa, K.; Yamabe, T.; Hoffmann, R. *New J. Chem.* **1997**, *21*, 151–161.
(720) Herold, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 145–156.
(721) Martens, C. F.; Murthy, N. N.; Obias, H. V.; Karlin, K. D. *Chem. Commun.* **1996**, 629–630.
(722) Nivorozhkin, A. L.; Anxolabéhère-Mallart, E.; Mialane, P.; Davydov, R.; Guilhem, J.; Cesario, M.; Audière, J.-P.; Girerd, J.-J.; Styring, S.; Schussler, L.; Seris, J.-L. *Inorg. Chem.* **1997**, *36*, 846–853.
(723) Duboc-Toia, C.; Ménage, S.; Ho, R. Y. N.; Que, L., Jr.; Lambeaux, C.; Fontecave, M. *Inorg. Chem.* **1999**, *38*, 1261–1268.
(724) Siegbahn, P. E. M.; Blomberg, M. R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 221–249.
(725) Knops-Gerrits, P.-P.; Jacobs, P. A.; Fukuoka, A.; Ichikawa, M.; Faglioni, F.; Goddard, W. A., III *J. Mol. Catal.* **2001**, *166*, 3–13.
(726) Siegbahn, P. E. M.; Crabtree, R. H.; Nordlund, P. *J. Biol. Inorg. Chem.* **1998**, *3*, 314–317.
(727) Mizuno, N.; Seki, Y.; Nishiyama, Y.; Kiyoto, I.; Misono, M. *J. Catal.* **1999**, *184*, 550–552.
(728) Trukhan, V. M.; Polukhov, V. V.; Sulimenkov, I. V.; Ovanesyan, N. S.; Koval′chuk, N. A.; Dodonov, A. F.; Shteinman, A. A. *Kinet. Catal.* **1998**, *39*, 788–791.
(729) Yoshizawa, K.; Ohta, K.; Yamabe, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1997**, *119*, 12311–12321.
(730) Gherman, B. F.; Dunietz, B. D.; Whittington, D. A.; Lippard, S. J.; Friesner, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 3836–3837.
(731) Dubkov, K. A.; Sobolev, V. I.; Talsi, E. P.; Rodkin, M. A.; Watkins, N. H.; Shteinman, A. A.; Panov, G. I. *J. Mol. Catal.* **1997**, *123*, 155–161.
(732) Yoshizawa, K. *J. Inorg. Biochem.* **2000**, *78*, 23–34.
(733) Kitajima, N.; Ito, M.; Fukui, H.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 102–104.
(734) Kitajima, N.; Fukui, H.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 485–486.
(735) Nishino, S.; Hosomi, H.; Ohba, S.; Matsushima, H.; Tokii, T.; Nishida, Y. *J. Chem. Soc., Dalton Trans.* **1999**, 1509–1513.
(736) Brandts, J. A. M.; Janssen, M. D.; Hogerheide, M. P.; Boersma, J.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1999**, *291*, 326–332.
(737) Ito, S.; Okuno, T.; Matsushima, H.; Tokii, T.; Nishida, Y. *J. Chem. Soc., Dalton Trans.* **1996**, 4479–4484.
(738) Wang, Z.; Martell, A. E.; Motekaitis, R. J. *Chem. Commun.* **1998**, 1523–1524.
(739) Shteinman, A. A. *J. Biol. Inorg. Chem.* **1998**, *3*, 325–330.
(740) Karasevich, E. I.; Kulikova, V. S.; Shilov, A. E.; Shteinman, A. A. *Russ. Chem. Rev.* **1998**, *67*, 376–398.
(741) Frey, P. A. *Chem. Rev.* **1990**, *90*, 1343–1357.
(742) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3103–3111.
(743) Basch, H.; Mogi, K.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1999**, *121*, 7249–7256.
(744) Siegbahn, P. E. M. *Inorg. Chem.* **1999**, *38*, 2880–2889.
(745) Siegbahn, P. E. M. *J. Biol. Inorg. Chem.* **2001**, *6*, 27–45.
(746) Brazeau, B. J.; Lipscomb, J. D. *Biochemistry* **2000**, *39*, 13503–13515.
(747) Chan, S. I. *J. Inorg. Biochem.* **1999**, *74*, 17.
(748) Priestley, N. D.; Floss, H. G.; Froland, W. A.; Lipscomb, J. D.; Williams, P. G.; Morimoto, H. *J. Am. Chem. Soc.* **1992**, *114*, 7561–7562.
(749) Rataj, M. J.; Kauth, J. E.; Donnelly, M. I. *J. Biol. Chem.* **1991**, *266*, 18684–18690.
(750) Elliott, S. J.; Zhu, M.; Tso, L.; Nguyen, H.-H. T.; Yip, J. H.-K.; Chan, S. I. *J. Am. Chem. Soc.* **1997**, *119*, 9949–9955.
(751) Valentine, A. M.; Le Tadic-Biadatti, M. H.; Toy, P. H.; Newcomb, M.; Lippard, S. J. *J. Biol. Chem.* **1999**, *274*, 10771–10776.
(752) Jin, Y.; Lipscomb, J. D. *Biochim. Biophys. Acta* **2000**, *1543*, 47–59.
(753) Liu, K. E.; Johnson, C. C.; Newcomb, M.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 939–947.
(754) Jin, Y.; Lipscomb, J. D. *Biochemistry* **1999**, *38*, 6178–6186.
(755) Choi, S.-Y.; Eaton, P. E.; Kopp, D. A.; Lippard, S. J.; Newcomb, M.; Shen, R. N. *J. Am. Chem. Soc.* **1999**, *121*, 12198–12199.
(756) Nesheim, J. C.; Lipscomb, J. D. *J. Inorg. Biochem.* **1995**, *59*, 369.
(757) Austin, R. N.; Chang, H.-K.; Zylstra, G. J.; Groves, J. T. *J. Am. Chem. Soc.* **2000**, *122*, 11747–11748.
(758) Patz, M.; Fukuzumi, S. *J. Phys. Org. Chem.* **1997**, *10*, 129–137.
(759) Hubig, S. M.; Rathore, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 617–626.
(760) Inada, T. N.; Miyazawa, C. S.; Kikuchi, K.; Yamauchi, M.; Nagata, T.; Takahashi, Y.; Ikeda, H.; Miyashi, T. *J. Am. Chem. Soc.* **1999**, *121*, 7211–7219.
(761) Karki, S. B.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Zona, T. A. *J. Am. Chem. Soc.* **1997**, *119*, 431–432.
(762) Trifunac, A. D.; Loffredo, D. M.; Liu, A.-D. *Radiat. Phys. Chem.* **1993**, *42*, 967–972.
(763) Mella, M.; Freccero, M.; Albini, A. *Tetrahedron* **1996**, *52*, 5533–5548.
(764) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290–4301.
(765) Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 1688–1694.
(766) Gerson, F. *Acc. Chem. Res.* **1994**, *27*, 63–69.

(767) Trifunac, A. D.; Sauer, M. C.; Shkrob, I. A.; Werst, D. W. *Acta Chem. Scand.* **1997**, *51*, 158−166.
(768) Werst, D. W.; Trifunac, A. D. *Acc. Chem. Res.* **1998**, *31*, 651−657.
(769) Werst, D. W.; Trifunac, A. D. *Radiat. Phys. Chem.* **1993**, *41*, 127−133.
(770) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2551−2589.
(771) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 5700−5702.
(772) Jahn, H. A.; Teller, E. *Phys. Rev.* **1936**, *49*, 874.
(773) Bersuker, I. B. *Chem. Rev.* **2001**, *101*, 1067−1114.
(774) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792−1795.
(775) Zhang, X. M.; Bordwell, F. G. *J. Org. Chem.* **1992**, *57*, 4163−4168.
(776) Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290−12295.
(777) de Lijser, H. J. P.; Arnold, D. R. *J. Phys. Chem.* **1996**, *100*, 3996−4010.
(778) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343−350.
(779) Linker, T.; Schmittel, M. *Radikale und Radikalionen in der Organischen Synthese*; Wiley-VCH: Weinheim, 1998.
(780) Traeger, J. C.; McAdoo, D. J.; Hudson, C. E.; Giam, C. S. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 21−28.
(781) Gaillard, E. R.; Whitten, D. G. *Acc. Chem. Res.* **1996**, *29*, 292−297.
(782) Sulzbach, H. M.; Graham, D.; Stephens, J. C.; Schaefer, H. F. *Acta Chem. Scand.* **1997**, *51*, 547−555.
(783) Sodupe, M.; Bertran, J.; Rodriguez-Santiago, L.; Baerends, E. J. *J. Phys. Chem. A* **1999**, *103*, 166−170.
(784) Wang, J. H.; Becke, A. D.; Smith, V. H. *J. Chem. Phys.* **1995**, *102*, 3477−3480.
(785) Laming, G. J.; Handy, N. C.; Amos, R. D. *Mol. Phys.* **1993**, *80*, 1121−1134.
(786) Clark, T. *Top. Curr. Chem.* **1996**, *177*, 1−23.
(787) Murray, C. W.; Handy, N. C. *J. Chem. Phys.* **1992**, *97*, 6509−6516.
(788) Ma, N. L.; Smith, B. J.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1991**, *113*, 7903−7912.
(789) Bally, T.; Bernhard, S.; Matzinger, S.; Truttmann, L.; Zhu, Z.; Roulin, J.-L.; Marcinek, A.; Gebicki, J.; Williams, F.; Chen, G.-F.; Roth, H. D.; Herbertz, T. *Chem. Eur. J.* **2000**, *6*, 849−857.
(790) Bally, T.; Truttmann, L.; Dai, S.; Williams, F. *J. Am. Chem. Soc.* **1995**, *117*, 7916−7922.
(791) Sastry, G. N.; Bally, T.; Hrouda, V.; Cársky, P. *J. Am. Chem. Soc.* **1998**, *120*, 9323−9334.
(792) Schreiner, P. R.; Wittkopp, A.; Gunchenko, P. A.; Yaroshinsky, A. I.; Peleshanko, S. A.; Fokin, A. A. *Chem. Eur. J.* **2001**, *7*, 2739−2744.
(793) Katriel, J.; Davidson, E. R. *Chem. Phys. Lett.* **1980**, *76*, 259−262.
(794) Arents, J.; Allen, L. C. *J. Chem. Phys.* **1970**, *53*, 73−78.
(795) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947−4955.
(796) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808−815.
(797) Meyer, W. *J. Chem. Phys.* **1973**, *58*, 1017−1035.
(798) Takeshita, K. *J. Chem. Phys.* **1987**, *86*, 329−338.
(799) Reeves, M. S.; Davidson, E. R. *J. Chem. Phys.* **1991**, *95*, 6551−6561.
(800) Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21−36.
(801) Eriksson, L. A.; Lunell, S.; Boyd, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 6896−6900.
(802) Paddon-Row, M. N.; Fox, D. J.; Pople, J. A.; Houk, K. N.; Pratt, D. W. *J. Am. Chem. Soc.* **1985**, *107*, 7696−7700.
(803) Boyd, R. J.; Darvesh, K. V.; Fricker, P. D. *J. Chem. Phys.* **1991**, *94*, 8083−8088.
(804) Frey, R. F.; Davidson, E. R. *J. Chem. Phys.* **1988**, *88*, 1775−1785.
(805) Knight, L. B., Jr.; Steadman, J.; Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 3700−3701.
(806) Matsushita, M.; Momose, T.; Shida, T.; Knight, L. B., Jr. *J. Chem. Phys.* **1995**, *103*, 3367−3376.
(807) Knight, L. B., Jr.; King, G. M.; Petty, J. T.; Matsushita, M.; Momose, T.; Shida, T. *J. Chem. Phys.* **1995**, *103*, 3377−3385.
(808) Signorell, R.; Sommavilla, M.; Merkt, F. *Chem. Phys. Lett.* **1999**, *312*, 139−148.
(809) Eriksson, L. A.; Wang, J.; Boyd, R. J. *Chem. Phys. Lett.* **1993**, *211*, 88−93.
(810) Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Phys. Lett.* **1999**, *311*, 281−291.
(811) Wetmore, S. D.; Boyd, R. J.; Eriksson, L. A.; Laaksonen, A. *J. Chem. Phys.* **1999**, *110*, 12059−12069.
(812) Brundle, C. R.; Robin, M. B.; Basch, H. *J. Chem. Phys.* **1970**, *53*, 2196−2213.
(813) Pullen, B. P.; Carlson, T. A.; Moddeman, W. E.; Schweitzer, G. K.; Bull, W. E.; Grimm, F. A. *J. Chem. Phys.* **1970**, *53*, 768−781.
(814) Signorell, R.; Merkt, F. *J. Chem. Phys.* **1999**, *110*, 2309−2311.
(815) Weitzel, K.-M.; Mähnert, J.; Baumgärtel, H. *Ber. Bun. Phys. Chem.* **1993**, *97*, 134−139.
(816) Weitzel, K.-M.; Malow, M.; Jarvis, G. K.; Baer, T.; Song, Y.; Ng, C. Y. *J. Chem. Phys.* **1999**, *111*, 8267−8270.
(817) Peko, B. L.; Dyakov, I. V.; Champion, R. L. *J. Chem. Phys.* **1998**, *109*, 5269−5275.
(818) Olah, G. A.; Lin, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1259−1261.
(819) Olah, G. A.; Ramaiah, P.; Rao, C. B.; Sandford, G.; Golam, R.; Trivedi, N. J.; Olah, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 7246−7249.
(820) French, M.; Kebarle, P. *Can. J. Chem.* **1975**, *53*, 2268−2274.
(821) Kim, S.-J.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Phys. Chem.* **1993**, *97*, 12232−12238.
(822) Mota, C. J. A.; Esteves, P. M.; Ramírez-Solís, A.; Hernández-Lamoneda, R. *J. Am. Chem. Soc.* **1997**, *119*, 5193−5199.
(823) Carneiro, J. W. M.; Schleyer, P. v. R.; Saunders, M.; Remington, R.; Schaefer, H. F.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 3483−3493.
(824) Schreiner, P. R.; Kim, S.-J.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716−3720.
(825) Schreiner, P. R. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3239−3241.
(826) Goeppert, A.; Sassi, A.; Sommer, J.; Esteves, P. M.; Mota, C. J. A.; Karlsson, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1999**, *121*, 10628−10629.
(827) Sommer, J.; Bukala, J.; Hachoumy, M.; Jost, R. *J. Am. Chem. Soc.* **1997**, *119*, 3274−3279.
(828) Farcasiu, D.; Lukinskas, P. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2295−2301.
(829) Sommer, J.; Bukala, J.; Hachoumy, M. *Res. Chem. Intermed.* **1996**, *22*, 753−766.
(830) Luzgin, M. V.; Stepanov, A. G.; Sassi, A.; Sommer, J. *Chem. Eur. J.* **2000**, *6*, 2368−2376.
(831) Collins, S. J.; O'Malley, P. J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4347−4355.
(832) Esteves, P. M.; Alberto, G. G. P.; Ramírez-Solís, A.; Mota, C. J. A. *J. Am. Chem. Soc.* **1999**, *121*, 7345−7348.
(833) Hiraoka, K.; Mori, T.; Yamabe, S. *Chem. Phys. Lett.* **1993**, *207*, 178−184.
(834) Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1993**, *115*, 9659−9666.
(835) Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 1336−1343.
(836) Bach, R. D.; Andrés, J. L.; Su, M.-D.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5768−5775.
(837) Bach, R. D.; Su, M.-D. *J. Am. Chem. Soc.* **1994**, *116*, 10103−10109.
(838) Decker, B. K.; Adams, N. G.; Babcock, L. M. *Int. J. Mass. Spectrosc.* **2000**, *195/196*, 185−201.
(839) Olah, G. A.; Hartz, N.; Rasul, G.; Wang, Q.; Prakash, G. K. S.; Casanova, J.; Christe, K. O. *J. Am. Chem. Soc.* **1994**, *116*, 5671−5673.
(840) Fang, W. H.; Peyerimhoff, S. D. *Mol. Phys.* **1998**, *93*, 329−339.
(841) Wang, Z.-X.; Huang, M.-B. *J. Am. Chem. Soc.* **1998**, *120*, 6758−6760.
(842) DePuy, C. H.; Gareyev, R.; Hankin, J.; Davico, G. E.; Krempp, M.; Damrauer, R. *J. Am. Chem. Soc.* **1998**, *120*, 5086−5092.
(843) Cacace, F.; de Petris, G.; Pepi, F.; Rosi, M.; Troiani, A. *Chem. Eur. J.* **1999**, *5*, 2750−2756.
(844) de Petris, G.; Pepi, F.; Rosi, M. *Chem. Phys. Lett.* **1999**, *304*, 191−196.
(845) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478−1486.
(846) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564.
(847) Mylvaganam, K.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1999**, *121*, 4633−4639.
(848) Chen, Y.-M.; Clemmer, D. E.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 7815−7826.
(849) Yoshizawa, K.; Shiota, Y.; Yamabe, T. *J. Am. Chem. Soc.* **1998**, *120*, 564−572.
(850) Yoshizawa, K.; Shiota, Y.; Yamabe, T. *Organometallics* **1998**, *17*, 2825−2831.
(851) Shimizu, K.; Okada, F.; Nakamura, Y.; Satsuma, A.; Hattori, T. *J. Catal.* **2000**, *195*, 151−160.
(852) Chen, Y.-M.; Sievers, M. R.; Armentrout, P. B. *Int. J. Mass. Spectrosc.* **1997**, *167/168*, 195−212.
(853) Yoshizawa, K.; Suzuki, A.; Yamabe, T. *J. Am. Chem. Soc.* **1999**, *121*, 5266−5273.
(854) Zhang, X.-G.; Liyanage, R.; Armentrout, P. B. *J. Am. Chem. Soc.* **2001**, *123*, 5563−5575.
(855) Yoshizawa, K. *J. Organomet. Chem.* **2001**, *635*, 100−109.
(856) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550−557.
(857) Olah, G. A.; Gupta, B.; Farina, M.; Felberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Melhotra, A. K.; Trivedi, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 7097−7105.
(858) Lin, M. R.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1996**, *118*, 4574−4580.

(859) Lunell, S.; Huang, M.-B. *J. Chem. Soc., Chem. Commun.* **1989**, 1031−1033.

(860) Eriksson, L. A.; Lunell, S. *J. Phys. Chem.* **1993**, *97*, 12215−12219.

(861) Huang, M.-B.; Lunell, S. *Chem. Phys.* **1990**, *147*, 85−90.

(862) Lunell, S.; Eriksson, L. A.; Huang, M.-B. *J. Mol. Struct. (THEOCHEM)* **1991**, *230*, 263−268.

(863) Ioffe, A.; Shaik, S. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1461−1473.

(864) Hudson, C. E.; McAdoo, D. J.; Giam, C. S. *J. Comput. Chem.* **1996**, *17*, 1532−1540.

(865) Zuilhof, H.; Dinnocenzo, J. P.; Reddy, A. C.; Shaik, S. *J. Phys. Chem.* **1996**, *100*, 15774−15784.

(866) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Chem. Phys.* **1982**, *77*, 5891−5912.

(867) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (S1), 1−872.

(868) Köppel, H.; Cederbaum, L. S.; Domcke, W.; Shaik, S. S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 210−224.

(869) Jursic, B. S. *J. Mol. Struct. (THEOCHEM)* **1998**, *452*, 145−152.

(870) Kurosaki, Y.; Takayanagi, T. *Chem. Phys. Lett.* **1997**, *277*, 291−298.

(871) Weitzel, K.-M.; Mähnert, J.; Baumgärtel, H. *Ber. Bun. Phys. Chem.* **1993**, *97*, 134−139.

(872) Mähnert, J.; Güthe, F.; Weitzel, K.-M. *Ber. Bun. Phys. Chem.* **1996**, *100*, 1899−1905.

(873) Baer, T. *Int. J. Mass. Spectrosc.* **2000**, *200*, 443−457.

(874) Güthe, F.; Weitzel, K.-M. *Ber. Bun. Phys. Chem.* **1997**, *101*, 484−490.

(875) Güthe, F.; Malow, M.; Weitzel, K.-M.; Baumgärtel, H. *Int. J. Mass. Spectrosc.* **1998**, *172*, 47−55.

(876) (a) Spanel, P.; Smith, D. *Int. J. Mass. Spectrosc.* **1998**, *181*, 1−10. (b) Schreiner, R. R.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1995**, *117*, 453−461.

(877) Arnold, S. T.; Viggiano, A. A.; Morris, R. A. *J. Phys. Chem.* **1997**, *101*, 9351−9358.

(878) Holthausen, M. C.; Koch, W. *J. Am. Chem. Soc.* **1996**, *118*, 9932−9940.

(879) Orlinkov, A. V.; Akhrem, I. S.; Vitt, S. V. *Mendeleev Commun.* **1999**, 198−199.

(880) Stolarov, I. P.; Vargaftik, M. N.; Shishkin, D. I.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1991**, 938−939.

(881) Pross, A. *J. Am. Chem. Soc.* **1986**, *108*, 3537−3538.

(882) Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1989**, *111*, 4306−4312.

(883) Shaik, S. S.; Shurki, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 587−625.

(884) Cho, J. K.; Shaik, S. *J. Am. Chem. Soc.* **1991**, *113*, 9890−9891.

(885) Shaik, S.; Reddy, A. C.; Ioffe, A.; Dinnocenzo, J. P.; Danovich, D.; Cho, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 3205−3222.

(886) Lunell, S.; Feller, D.; Davidson, E. R. *Theor. Chim. Acta* **1990**, *77*, 111−122.

(887) Olivella, S.; Solé, A.; McAdoo, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 9368−9376.

(888) Toriyama, K. *Chem. Phys. Lett.* **1991**, *177*, 39−44.

(889) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213−2233.

(890) Lifshitz, C.; Shapiro, M. *J. Chem. Phys.* **1966**, *45*, 4242−4248.

(891) Vestal, M.; Futrell, J. H. *J. Chem. Phys.* **1970**, *52*, 978−988.

(892) McAdoo, D. J.; Olivella, S.; Solé, A. *J. Phys. Chem.* **1998**, *102*, 10798−10804.

(893) Huang, M.-B.; Lunell, S. *J. Mol. Struct. (THEOCHEM)* **1990**, *205*, 317−325.

(894) Olivella, S.; Solé, A.; McAdoo, D. J.; Griffin, L. L. *J. Am. Chem. Soc.* **1994**, *116*, 11078−11088.

(895) Mead, P. T.; Donchi, K. F.; Traeger, J. C.; Christie, J. R.; Derrick, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3364−3369.

(896) Holmes, J. L.; Wolkoff, P.; Rye, R. T. B. *J. Chem. Soc., Chem. Commun.* **1979**, 544−545.

(897) Liu, Y.-J.; Huang, M.-B. *Chem. Phys. Lett.* **2000**, *321*, 89−94.

(898) Wolkoff, P.; Holmes, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 7346−7352.

(899) Holmes, J. L.; Burgers, P. C.; Mollah, M. Y. A.; Wolkoff, P. *J. Am. Chem. Soc.* **1982**, *104*, 2879−2884.

(900) Toriyama, K.; Okazaki, M.; Nunome, K.; Matsuura, K. *Radiat. Phys. Chem.* **1991**, *37*, 15−21.

(901) Ichikawa, T.; Ohta, N.; Shiotani, M. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2901−2904.

(902) Ichikawa, T.; Yoshida, H. *J. Phys. Chem.* **1992**, *96*, 7656−7661.

(903) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Am. Chem. Soc.* **1987**, *109*, 4496−4500.

(904) Stienlet, D.; Ceulemans, J. *J. Phys. Chem.* **1992**, *96*, 8751−8756.

(905) Demeyer, A.; Stienlet, D.; Ceulemans, J. *J. Phys. Chem.* **1994**, *98*, 5830−5843.

(906) Ceulemans, J. *Spectrochim. Acta, A* **1998**, *54*, 2359−2372.

(907) Slabbinck, L.; Demeyer, A.; Ceulemans, J. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2241−2247.

(908) Stienlet, D.; Ceulemans, J. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1449−1453.

(909) Demeyer, A.; Ceulemans, J. *J. Phys. Chem.* **2000**, *104*, 4004−4010.

(910) Demeyer, A.; Ceulemans, J. *J. Phys. Chem.* **1997**, *101*, 3537−3541.

(911) Miyazaki, T.; Kitamura, S.; Kozono, Y.; Matsunaga, H. *J. Phys. Chem.* **1994**, *98*, 10767−10770.

(912) Kurosaki, Y.; Takayanagi, T.; Miyazaki, T. *J. Mol. Struct. (THEOCHEM)* **1998**, *452*, 209−218.

(913) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405−3412.

(914) Lunell, S.; Yin, L.; Huang, M.-B. *Chem. Phys.* **1989**, *139*, 293−299.

(915) Krogh-Jespersen, K.; Roth, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 8388−8394.

(916) Ohta, K.; Nakatsuji, H.; Kubodera, H.; Shida, T. *Chem. Phys.* **1983**, *76*, 271−281.

(917) Eriksson, L. A.; Lunell, S. *J. Am. Chem. Soc.* **1992**, *114*, 4532−4535.

(918) Skancke, A. *J. Phys. Chem.* **1995**, *99*, 13886−13889.

(919) Liu, Y.-J.; Huang, M.-B. *J. Mol. Struct. (THEOCHEM)* **2001**, *536*, 133−142.

(920) Qin, X.-Z.; Williams, F. *Tetrahedron* **1986**, *42*, 6301−6314.

(921) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202−204.

(922) Dinnocenzo, J. P.; Merchán, M.; Roos, B. O.; Shaik, S.; Zuilhof, H. *J. Phys. Chem.* **1998**, *102*, 8979−8987.

(923) Roth, H. D.; Herbertz, T.; Lakkaraju, P. S.; Sluggett, G.; Turro, N. J. *J. Phys. Chem.* **1999**, *103*, 11350−11354.

(924) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283−3289.

(925) Sack, T. M.; Miller, D. L.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 6795−6800.

(926) Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649−1665.

(927) Shaik, S.; Dinnocenzo, J. P. *J. Org. Chem.* **1990**, *55*, 3434−3436.

(928) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462−2464.

(929) Dinnocenzo, J. P.; Zuilhof, H.; Lieberman, D. R.; Simpson, T. R.; McKechney, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 994−1004.

(930) Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6828−6829.

(931) Gassman, P. G.; Burns, S. J. *J. Org. Chem.* **1988**, *53*, 5576−5578.

(932) Herbertz, T.; Roth, H. D. *J. Am. Chem. Soc.* **1996**, *118*, 10954−10962.

(933) Dinnocenzo, J. P.; Lieberman, D. R.; Simpson, T. R. *J. Am. Chem. Soc.* **1993**, *115*, 366−367.

(934) Dinnocenzo, J. P.; Simpson, T. R.; Zuilhof, H.; Todd, W. P.; Heinrich, T. *J. Am. Chem. Soc.* **1997**, *119*, 987−993.

(935) Bergmark, W.; Hector, S.; Jones, G.; Oh, C.; Kumagai, T.; Hara, S.; Segawa, T.; Tanaka, N.; Mukai, T. *J. Photochem. Photobiol.* **1997**, *109*, 119−124.

(936) Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *J. Org. Chem.* **1992**, *57*, 4669−4673.

(937) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378−2382.

(938) Jungwirth, P.; Cársky, P.; Bally, T. *J. Am. Chem. Soc.* **1993**, *115*, 5776−5782.

(939) Wiest, O. *J. Phys. Chem.* **1999**, *103*, 7907−7911.

(940) Ushida, K.; Shida, T.; Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Am. Chem. Soc.* **1983**, *105*, 5496−5497.

(941) Scattel, N. J.; Oxgaard, J.; Wiest, O. *Eur. J. Org. Chem.* **2001**, 1429−1439.

(942) Tabata, M.; Lund, A. *Chem. Phys.* **1983**, *75*, 379−388.

(943) Iwasaki, M.; Toriyama, K.; Nunome, K. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 19−33.

(944) Sjöqvist, L.; Lund, A.; Maruani, J. *Chem. Phys.* **1988**, *125*, 293−298.

(945) Lunell, S.; Eriksson, L. A.; Fängström, T.; Maruani, J.; Sjöqvist, L.; Lund, A. *Chem. Phys.* **1993**, *171*, 119−131.

(946) Wang, P.; Shiotani, M.; Lunell, S. *Chem. Phys. Lett.* **1998**, *292*, 110−114.

(947) Lindgren, M.; Shiotani, M.; Ohta, N.; Ichikawa, T.; Sjoqvist, L. *Chem. Phys. Lett.* **1989**, *161*, 127−130.

(948) Shiotani, M.; Lindgren, M.; Ohta, N.; Ichikawa, T. *J. Chem. Soc., Perkin Trans. 2* **1991**, 711−719.

(949) Lindgren, M.; Matsumoto, M.; Shiotani, M. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1397−1402.

(950) Katsumura, Y.; Azuma, T.; Quadir, M. A.; Domazou, A. S.; Bühler, R. E. *J. Phys. Chem.* **1995**, *99*, 12814−12821.

(951) Shiotani, M.; Wang, P.; Komaguchi, K. *Bull. Pol. Acad. Sci.* **1999**, *47*, 89−100.

(952) Mella, M.; Freccero, M.; Albini, A. *J. Chem. Soc., Chem. Commun.* **1995**, 41−42.

(953) Mella, M.; Fagnoni, M.; Freccero, M.; Fasani, E.; Albini, A. *Chem. Soc. Rev.* **1998**, *27*, 81−89.

(954) Shkrob, I. A.; Sauer, M. C.; Trifunac, A. D. *J. Phys. Chem.* **1996**, *100*, 7237−7245.

(955) Sauer, M. C.; Shkrob, I. A.; Yan, J.; Schmidt, K.; Trifunac, A. D. *J. Phys. Chem.* **1996**, *100*, 11325−11335.

(956) Shkrob, I. A.; Sauer, M. C.; Yan, J.; Trifunac, A. D. *J. Phys. Chem.* **1996**, *100*, 6876−6878.

(957) Shkrob, I. A.; Sauer, M. C.; Trifunac, A. D. *J. Phys. Chem.* **1999**, *103*, 3, 4773−4780.

(958) Anisimov, O. A.; Warman, J. M.; de Haas, M. P.; de Leng, H. *Chem. Phys. Lett.* **1987**, *137*, 365−368.

(959) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1992**, *96*, 9189−9194.

(960) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1989**, *111*, 6456−6457.

(961) Barone, V.; Rega, N.; Bally, T.; Sastry, G. N. *J. Phys. Chem.* **1999**, *103*, 217−219.

(962) Abelt, C. J.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4148−4152.

(963) Gassman, P. G.; Hay, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 4075−4076.

(964) Gassman, P. G.; Hay, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 4227−4228.

(965) Hoz, S.; Livneh, M.; Cohen, D. *J. Am. Chem. Soc.* **1987**, *109*, 5149−5156.

(966) Blancafort, L.; Adam, W.; González, D.; Olivucci, M.; Vreven, T.; Robb, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 10583−10590.

(967) Adam, W.; Corma, A.; Miranda, M. A.; Sabater-Picot, M.-J.; Sahin, C. *J. Am. Chem. Soc.* **1996**, *118*, 2380−2386.

(968) Williams, F.; Guo, Q.-X.; Kolb, T. M.; Nelsen, S. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1835−1837.

(969) Adam, W.; Heidenfelder, T. *J. Am. Chem. Soc.* **1998**, *120*, 11858−11863.

(970) Adam, W.; Handmann, V.-I.; Kita, F.; Heidenfelder, T. *J. Am. Chem. Soc.* **1998**, *120*, 831−832.

(971) Adam, W.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007−3014.

(972) Adam, W.; Sahin, C.; Sendelbach, J.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1994**, *116*, 2576−2584.

(973) Adam, W.; Sahin, C. *Tetrahedron Lett.* **1994**, *35*, 9027−9030.

(974) Wiberg, K. B.; Walker, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239−5240.

(975) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379−386.

(976) Honegger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7172−7174.

(977) Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820−5828.

(978) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4132−4139.

(979) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779−786.

(980) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591−599.

(981) Gleiter, R.; Spanget-Larsen, J. In *Advances in Strain in Organic Chemistry*; JAI Press Ltd.: London, 1992; Vol. 2, pp 143−189.

(982) Fokin, A. A.; Schreiner, P. R.; Schleyer, P. v. R.; Gunchenko, P. A. *J. Org. Chem.* **1998**, *63*, 6494-6502.

(983) Alder, R. W.; Sessions, R. B.; Symons, M. C. R. *J. Chem. Res.* **1981**, 82−83.

(984) Fokin, A. A.; Gunchenko, P. A.; Peleshanko, S. A.; Schleyer, P. v. R.; Schreiner, P. R. *Eur. J. Org. Chem.* **1999**, 855860.

(985) Fokin, A. A.; Gunchenko, P. A.; Kulik, N. I.; Iksanova, S. V.; Krasutsky, P. A.; Gogoman, I. V.; Yurchenko, A. G. *Tetrahedron* **1996**, *52*, 5857−5866.

(986) Bren, V. A.; Dubonosov, A. D.; Minkin, V. I.; Chernoivanov, V. A. *Usp. Khim.* **1991**, *60*, 913−948.

(987) Rosi, M.; Sgamellotti, A.; Franceschi, F.; Floriani, C. *Inorg. Chem.* **1999**, *38*, 1520−1522.

(988) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583−592.

(989) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180−186.

(990) Chen, G.-F.; Wang, J. T.; Williams, F.; Belfield, K. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 9853−9855.

(991) Bühler, R. E.; Quadir, M. A. *J. Phys. Chem.* **2000**, *104*, 2634−2640.

(992) Adam, W.; Heidenfelder, T.; Sahin, C. *J. Am. Chem. Soc.* **1995**, *117*, 9693−9698.

(993) White, K.; Buttry, D. A. *J. Electrochem. Soc.* **2000**, *147*, 266−271.

(994) Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392−4393.

(995) Bach, R. D.; Schilke, I. L.; Schlegel, H. B. *J. Org. Chem.* **1996**, *61*, 4845−4847.

(996) Ishiguro, K.; Khudyakov, I. V.; McGarry, P. F.; Turro, N. J.; Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 6933−6934.

(997) Clark, T. *Acta Chem. Scand.* **1997**, *51*, 646−652.

(998) Inadomi, Y.; Morihashi, K.; Kikuchi, O. *J. Mol. Struct. (THEOCHEM)* **1998**, *434*, 59−66.

(999) Herges, R.; Starck, F.; Winkler, T.; Schmittel, M. *Chem. Eur. J.* **1999**, *5*, 2965−2970.

(1000) Gebicki, J. L.; Gebicki, J.; Mayer, J. *Radiat. Phys. Chem.* **1987**, *30*, 165−167.

(1001) McIlroy, S.; Weng, H. X.; Roth, H. D. *Tetrahedron Lett.* **1995**, *36*, 7829−7832.

(1002) Weng, H. X.; Roth, H. D. *J. Org. Chem.* **1995**, *60*, 4136−4145.

(1003) McIlroy, S.; Weng, H. X.; Roth, H. D. *J. Phys. Org. Chem.* **1997**, *10*, 607−611.

(1004) Du, X. Y.; Arnold, D. R.; Boyd, R. J.; Shi, Z. *Can. J. Chem.* **1991**, *69*, 1365−1375.

(1005) Goez, M.; Frisch, I. *J. Am. Chem. Soc.* **1995**, *117*, 10486−10502.

(1006) Cuppoletti, A.; Dinnocenzo, J. P.; Goodman, J. L.; Gould, I. R. *J. Phys. Chem.* **1999**, *103*, 11253−11256.

(1007) Prinzbach, H.; Murty, B. A. R. C.; Fessner, W.-D.; Mortensen, J.; Heinze, J.; Gescheidt, G.; Gerson, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 457−458.

(1008) Prinzbach, H.; Gescheidt, G.; Matrtin, H.-D.; Herges, R.; Heinze, J.; Surya Prakash, G. K.; Olah, G. A. *Pure Appl. Chem.* **1995**, *67*, 673−682.

(1009) Prinzbach, H.; Wollenweber, M.; Herges, R.; Neumann, H.; Gescheidt, G.; Schmidlin, R. *J. Am. Chem. Soc.* **1995**, *117*, 1439−1440.

(1010) Gescheidt, G.; Herges, R.; Neumann, H.; Heinze, J.; Wollenweber, M.; Etzkorn, M.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1016−1019.

(1011) Gescheidt, G.; Prinzbach, H.; Davies, A. G.; Herges, R. *Acta Chem. Scand.* **1997**, *51*, 174−180.

(1012) Trifunac, A. D.; Werst, D. W.; Herges, R.; Neumann, H.; Prinzbach, H.; Etzkorn, M. *J. Am. Chem. Soc.* **1996**, *118*, 9444−9445.

(1013) Prinzbach, H.; Reinbold, J.; Bertau, M.; Voss, T.; Martin, H.-D.; Mayer, B.; Heinze, J.; Neschchadin, D.; Gescheidt, G.; Prakash, G. K. S.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 911−914.

(1014) Etzkorn, M.; Wahl, F.; Keller, M.; Prinzbach, H.; Barbosa, F.; Peron, V.; Gescheidt, G.; Heinze, J.; Herges, R. *J. Org. Chem.* **1998**, *63*, 6080−6081.

(1015) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308−1310.

(1016) Griffin, G. W.; Marchand, A. P. *Chem. Rev.* **1989**, *89*, 997−1010.

(1017) Qin, X.-Z.; Trifunac, A. D.; Eaton, P. E.; Xiong, Y. *J. Am. Chem. Soc.* **1991**, *113*, 669−670.

(1018) Qin, X.-Z.; Trifunac, A. D.; Eaton, P. E.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 4565−4567.

(1019) Eaton, P. E.; Yang, C.-X.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3225−3226.

(1020) Marcinek, A.; Rogowski, J.; Gebicki, J.; Chen, G.-F.; Williams, F. *J. Phys. Chem.* **2000**, *104*, 5265−5268.

(1021) Mella, M.; Freccero, M.; Soldi, T.; Fasani, E.; Albini, A. *J. Org. Chem.* **1996**, *61*, 1413−1422.

(1022) Miller, L. L.; Koch, V. R. *Tetrahedron Lett.* **1973**, 693−696.

(1023) Koch, V. R.; Miller, L. L. *J. Am. Chem. Soc.* **1973**, *95*, 8631−8637.

(1024) Edwards, G. J.; Jones, S. R.; Mellor, J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 816−817.

(1025) Edwards, G. J.; Jones, S. R.; Mellor, J. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 505−510.

(1026) Stetter, H.; Wulff, C. *Chem. Ber.* **1960**, *93*, 1366−1371.

(1027) Yurchenko, A. G.; Kulik, N. I.; Kuchar, V. P.; Djyakovskaya, V. M.; Baklan, V. F. *Tetrahedron Lett.* **1986**, 1399−1402.

(1028) Moiseev, I. K.; Belyaev, P. G.; Barabanov, N. V.; Bardyug, O. P.; Vishnevskii, E. H.; Novatskaya, N. I.; Golod, E. L.; Gidaspov, B. V. *Zh. Org. Khim.* **1975**, *11*, 214−215.

(1029) Moiseev, I. K.; Klimochkin, Y. N.; Zemtsova, M. N.; Traktenberg, P. L. *Zh. Org. Khim.* **1984**, *20*, 1435−1438.

(1030) Olah, G. A.; Shih, J. G.; Singh, B. P.; Gupta, B. G. B. *J. Org. Chem.* **1983**, *48*, 3356−3358.

(1031) Bach, R. D.; Holubka, J. W.; Badger, R. C.; Rajan, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 4416−4417.

(1032) Akhrem, I.; Churilova, I.; Bernadyuk, S.; Vol′pin, M. *Tetrahedron Lett.* **1996**, *37*, 5775−5778.

(1033) Ishii, Y.; Matsunaka, K.; Sakaguchi, S. *J. Am. Chem. Soc.* **2000**, *122*, 7390−7391.

(1034) Moiseev, I. K.; Makarova, N. V.; Zemtsova, M. N. *Russ. Chem. Rev.* **1999**, *68*, 1001−1020.

(1035) Olah, G. A.; Ramaiah, P. *J. Org. Chem.* **1993**, *58*, 4639−4641.

(1036) Ridd, J. H. *Acta Chem. Scand.* **1998**, *52*, 11−22.

(1037) Tanaka, M.; Muro, E.; Ando, H.; Xu, Q.; Fujiwara, M.; Souma, Y.; Yamaguchi, Y. *J. Org. Chem.* **2000**, *65*, 2972−2978.

(1038) Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **2000**, *122*, 8279−8288.

(1039) Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *20*, 53−59.

(1040) Kochi, J. K. *Acc. Chem. Res.* **1992**, *25*, 39−47.

(1041) Sen, A.; Gretz, E.; Oliver, T. F.; Jiang, Z. *New J. Chem.* **1989**, *13*, 755−760.

(1042) Beattie, J. K.; Macleman, S.; Masters, A. F. *Inorg. Chim. Acta* **1999**, *294*, 99−102.

(1043) Yamanaka, I.; Furukawa, T.; Otsuka, K. *Chem. Commun.* **2000**, 2209−2210.

CR000453M