Thermochemistry and Kinetics of Ozonation Reactions

Prakash S. Nangia and Sidney W. Benson*

Contribution from the Hydrocarbon Research Institute and the Department of Chemistry, University of Southern California, Los Angeles, California 90007.
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Abstract: Empirical estimation methods of transition-state theory together with recent thermochemical data (both estimated and observed) are used to explore reaction pathways for ozonation reactions. For unsaturated compounds it is shown that all three steps in the formation of stable ozonides are fast, concerted processes. These are (a) primary ozonide formation, (b) cleavage of primary ozonide into carbonyl oxide plus aldehyde or ketone, and (c) recombination of carbonyl oxide with aldehyde (or ketone) to produce stable ozonide. Self-consistent Arrhenius parameters and thermochemistry are derived for each step. Scavenging experiments are shown to be consistent with about 60% cage recombination for process (c). The exothermicities of steps (a) and (c) are shown not to lead to hot molecule effects in liquid state, but can do so in gas reactions. These exothermicities do lead, however, to important self-heating in ozonation of olefins. Direct exchange of O-atom labeled aldehyde with ozone is shown to be kinetically feasible via a cyclic tetraoxide, metastable at ambient temperatures. Ozone reactions with saturated compounds are shown by contrast to all proceed via hydride ion transfer to form an intimate ion pair $[R^+HO_3^-]$ in a solvent cage which can exothermically collapse to the observed products RO_3H. Solvation enthalpies are calculated from the Kirkwood formula for dipole solvation and shown to lead to reasonable activation energies for ozonation of alkanes, alcohols, and acetals, all of which produce the hydrotrioxides. The kinetics of the subsequent decomposition of these species is shown to proceed via radical processes, including cage disproportionation, which is proposed as the source of the observed high yields of singlet O_2: $RO_3H \rightleftharpoons [R\dot{O}\cdots\dot{O}_2H] \rightarrow ROH + O_2(^1\Delta)$ (main path) (a); $[R\dot{O}\cdots\dot{O}_2H] \rightarrow R\dot{O} + H\dot{O}_2$ (followed by chain) (b); $[R\dot{O}\cdots\dot{O}_2H] \rightarrow$ aldehyde $+ H_2O_2$ (e). Rate constants are derived for these decompositions and also for the subsequent chain reactions initiated by the radicals which escape the cage (step b) in good agreement with observed data. It is shown that the extremely rapid scavenging reactions of carbonyl oxides by alcohols follow a proton transfer process: $R_2\overline{COO} + R'CH_2OH \rightleftharpoons [R_2COOH^+\cdots R'CH_2\overline{O}] \rightarrow R_2C(OOH)OCH_2R'$. Recent data on the t-$BuO_2H + O_3$ reaction also show it to be intiated by hydride ion transfer and O_2 elimination from HO_3^- to form t-$BuO_2^+\ OH^-$, which collapses to t-BuO_3H and then decomposes via the above radical mechanism.

Introduction

Over the past 3 decades intensive reseach on the kinetics and thermochemistry of free-radical reactions, both in the gas phase and in solution, has made it possible to deduce relatively consistent sets of rate constants for elementary reactions together with the thermochemistry and Arrhenius parameters for many of these reactions.[1] Parallel developments in transition-state theory have also made it possible to develop empirical methods for deducing A factors and activation energies for such reactions to within experimental accuracy.[2-4] Applying these methods systematically to the kinetics of oxidation reactions has permitted us recently to deduce consistent sets of Arrhenius parameters for both low- and high-temperature oxidation reactions[5-7] of hydrocarbons. An important factor in achieving this has been the systematic improvement in the knowledge of the thermochemistry of polyoxides and their free radicals.[5,8]

In the course of this work it has been possible to deduce the existence of a set of new, important reactive intermediates, the carbonyl oxides. These species with the general formula $R_1R_2C{=}O{\rightarrow}O$ were originally postulated by Criegee[9] to account for the mechanism of the interaction of ozone with olefins, and have been for a long time referred to as Criegee zwitterions because of their inferred electrophilic behavior. Ozone itself is a very reactive species capable of reacting with saturated organic molecules as well as with unsaturates but the detailed mechanism of these processes is somewhat uncertain.[10-12]

Because of the importance of ozone chemistry to the phenomenon of air pollution in the troposphere and to the stability of the ozone layer in the stratosphere as well as for its general research and industrial importance, there has been a renewed interest in the detailed mechanism of its reactions. In view also of its intimate relation to oxide and polyoxide species it seemed to us of particular interest to apply the techniques of thermochemistry and transition-state theory together with the information deduced from our work on polyoxides to try to reach a unique mechanism for the detailed reactions of ozone together with the intermediates involved therein. Finally, if this were possible, we hoped to be able to assign a consistent set of transition-state parameters to the elementary step reactions.

In the present paper we shall discuss the mechanism of the elementary steps involved in ozone reactions with olefins and the subsequent decomposition of the primary ozonides. Then we shall discuss the mechanism of ozonation of saturated compounds and the decomposition of the products. In the course of this we shall show that free-radical reactions play a minor role at temperatures below 0 °C and that concerted or heterolytic pathways provide the major reaction channels. To do this quantitatively we have borrowed heavily from the recent thermochemical data on positive and negative ions[13-15] and simple models for the solvation of ion pairs.[15,16]

Thermochemical Considerations

In the following, we consider the limitations that the thermochemical calculations place on the various possible modes of reactions during ozonolysis. In order to calculate the heats of formation of various entities for which no direct data is available, resort has been made to group additivity tables.[4,8] However, a new value for the $\Delta H_f°$ of the group $\overline{O}$-$(O)_2$ equal to 14.8 kcal/mol has been employed[17] in place of the older value[4] or the recently suggested value.[8] It is used in the estimation of $\Delta H_f°$ values for various species. For five-membered rings, a strain of 6 kcal/mol has been uniformly incorporated with zero for six-membered rings. The $\Delta H_f°$ values of the radicals or biradicals, as the case may be, are computed from the corresponding compounds by using known C-H, O-H, or RO_2-H bond energies, using estimated $\Delta H_f°$ values for the compounds, where not known, from group additivity tables. These are recorded in Table I, generally listing the molecules and the radicals derived therefrom in the same row. While the $\Delta H_f°$ listed pertain to the ideal gas state, it is known that in not too polar solvents net heats of reaction tend to be very close

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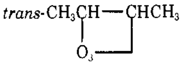
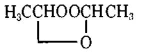
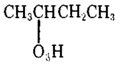
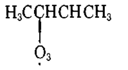
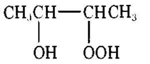
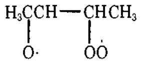
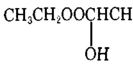
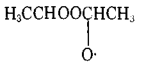
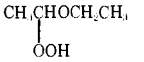
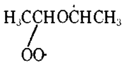
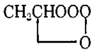
Table I. Heats of Formation of Molecules and Radicals[a]

compd	$\Delta H_f°$ [b]	compd or radical	$\Delta H_f°$[b]	DH°(C-H)[c]	$DH°(RO_n\text{-}H)$
O_3	34.1	$\cdot O\text{-}O\text{-}O\cdot$	53.0		
trans-C_4H_8	−2.7	CH_3CHO	−39.7		
CH_3CH_2OOH **3**	−39.0	$CH_3\overline{CHOO}$ **4**	14.0	91.0	87.6
 $trans\text{-}CH_3CH\text{—}CHCH_3$ (O_3 ring) **5**	−23.0	 $H_3CCHOOCHCH_3$ (ring via O) **6**	−79.2		
 $CH_3CH(O_3H)CH_2CH_3$ **7**	−39.2	 $H_3CCH(\dot{O}_3)CHCH_3$ **8**	39.2	95.0	87.6
 $CH_3CH(OH)\text{—}CH(OOH)CH_3$ **9**	−93.5	 $H_3CCH(O\cdot)\text{—}CH(\dot{O}O)CH_3$ **10**	−6.0		87.6
 $CH_3CH_2OOCH(OH)CH_3$ **11**	−91.7	 $H_3CCHOOCH(O\cdot)CH_3$ **12**	−0.9	91.0	104.0
 $CH_3CH(OOH)OCH_2CH_3$ **13**	−88.8	 $H_3CCH(OO\cdot)O\dot{C}HCH_3$ **14**	−14.4	91.0	87.6
 CH_3CHOOO (ring via O) **15**	0.0	HOOOH	−17.7		87.6
		$HO_3\cdot$	+17.8		68.4

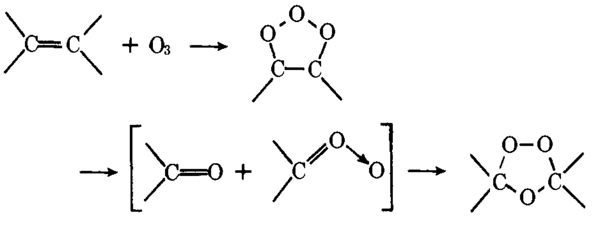
[a] The numbers below the species are used for future identification in the text. [b] All values in kcal/mol at 298 K for ideal gas state species (1 atm). [c] The bond-dissociation enthalpy of secondary H atoms, DH°(C-H), has been lowered by 4 kcal when C atom is linked to any oxygen atom as has been found for the bond-dissociation enthalpy in methanol, $DH°(H\text{-}CH_2OH)$.[15] A value $DH°(RO_n\text{-}H)$ = 87.6 kcal/mol is used for $n \geq 2$. [d] Based on a value of 37.4 kcal/mol deduced for the hypothetical biradical less a stabilization energy, Δ = 22.0 kcal/mol, as given in text.

to those in the gas phase.[3,18] Thus within possible uncertainties of 1-2 kcal/mol we shall be able to employ the $\Delta H_f°$ from Table I for calculating heats of reaction in solution again to about 1-2 kcal/mol. It should be noted that, even when $\Delta H_r°$ differ between liquid and gas phases, the net effect on the free-energy change tends to be compensated. Thus equilibrium and rate constants tend to be very similar even when $\Delta H_r°$ and ΔS_r (or the corresponding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) are individually different.[18,19]

The heats of formation of the carbonyl oxides $R_1R_2\overline{COO}$ and the 1,3-dioxo biradicals are taken from earlier work[6] and for the former are based on a stabilization energy of 22-23 kcal/mol varying with the nature of R_1 and R_2. This stabilization energy can be compared to a value of 19.2 kcal/mol in O_3 and a value of 17 kcal/mol calculated by Harding and Goddard[20] using ab initio methods plus group additivity. We have estimated $\Delta H_f°$ for carbonyl oxides to be uncertain by about ±2 kcal/mol, but even a larger uncertainty of ±5 kcal would not affect the conclusions arrived at later in our discussions of ozonation of olefins.

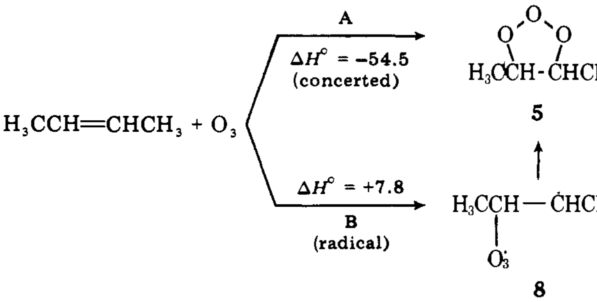
Formation of Primary Ozonides

The addition of O_3 to olefins is remarkably rapid even at −100 °C and the reaction is well documented as proceeding to a 1,2,3-trioxide ring compound[12] which appears to undergo subsequent rearrangement even at 200 K to the more stable 1,2,4-trioxolane (I).



(I)

In a typical case of *trans*-2-butene and ozone reactions, the two paths in eq II are possible for the first step. Using $\Delta H_f°$



(II)

values from Table I, it is found that path B involving the formation of biradical **8** would be prohibitively slow at temperatures below −70 °C (where the ozonation occurs rapidly) because of its endothermicity of 7.8 kcal/mol. Hence the addition must occur as a concerted process with a concomitant low *A* factor (path A). This has, in fact, been observed in the reaction of $C_2H_4 + O_3$ in gas phase by DeMore,[21] who from the measurement of the rate of disappearance of O_3 in the temperature range −95 to −40 °C deduced a second-order rate constant given by $\log k(M^{-1}\ s^{-1}) = 6.3 \pm 0.2 - (4.7 \pm 0.2)/\theta$ where $\theta = 2.303RT$ in kcal/mol. The expected *A* factor for a concerted reaction involving a tight transition state is calculable from transition-state theory[22] as $10^{6.5}\ M^{-1}\ s^{-1}$. In the following, the *A* factor adopted for such additions has been taken uniformly as $10^{6.5}\ M^{-1}\ s^{-1}$. If we scale DeMore's rate constant, this implies an increase in the activation energy to 5.0 kcal/mol for the above reaction. From the data on the relative reactivities of C_2H_4 and *trans*-C_4H_8-2 toward O_3 reported by Cvetanovic et al.,[23] ~1/9 at 298 K (gas phase), an activation energy lower by 1.3 or 3.7 kcal is deducible for *trans*-C_4H_8-2.

The method for measuring the relative reactivities was based on the yields of carbonyl compounds assumed to arise directly from the reactants and as such it precludes any complexity due to reactions of O atoms formed by decomposition of ozone, $O_3 + M \rightarrow O_2 + O + M$. This may not, however, be entirely correct. The complexity involved will be dealt with in a separate communication. Since the O-atom reactions with olefins are less discriminatory, it is expected that the concerted reaction of O_3 with *trans*-C_4H_8 could have a lower activation energy than that deduced above.

This is supported by the recent observations of Nelander and Nord,[24] who prepared mixtures of olefins plus ozone in glasses of Ar or N_2 in the range 10-90 K. They showed that all olefins except ethylene reacted with O_3 at 65 K or even lower. This suggests an activation energy near 2.5 kcal for 2-butene.

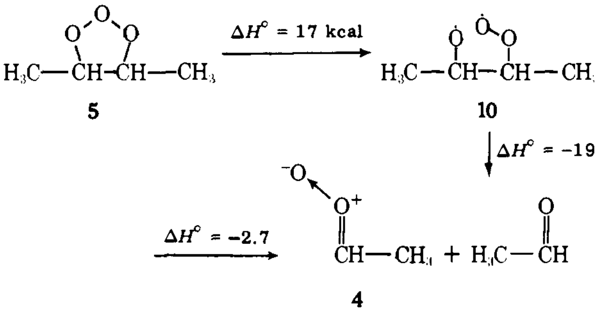
The formation of primary ozonide **5**, as shown above, is exothermic by 54.5 kcal/mol so that it would be a "hot" molecule containing ~58 kcal/mol (including an activation energy of 3.7 kcal). It is important to consider its stability vs. heat dissipation in the liquid-phase reaction. We have recently deduced[6] the Arrhenius parameters for the decomposition of primary *trans*-butene 2-ozonide, as $\log k\ (s^{-1}) = 13.0 - (12.5/\theta)$. From RRK theory, the lifetime τ of the "hot" ozonide (containing E = 58 kcal and with E_a +12.5 kcal) is found to be $\sim 10^{-10}$ s for a total number of effective oscillators, s = 29, where we have neglected all the eight C-H stretches and the two methyl internal rotations. The rate of heat dissipation can be described in terms of the time, t, to reach a steady state with the walls of the vessel which we take here to be the first layer of solvent molecules. The relation derived by Benson[25] is $t = r_0^2 \rho c_v/\pi^2 k$, where r_0 = radius of the vessel, ρ = density of liquid, c_v = its specific-heat, and k = its thermal conductivity. We take r_0 as the radius of solvent cage, estimated to be 9 Å when the ozonide undergoes decomposition and the fragments move apart to about 4-5 Å. The product ρc_v is 0.3 cal/cm^3·°C for both *n*-pentane and isopentane and $k \simeq 1.0 \times 10^{-3}$ cal/cm·s·°C. Substitution of various quantities leads to a value $t = 3 \times 10^{-13}$ s. Heat dissipation is thus faster by more than two orders of magnitude than reaction. This would not be the situation, however, in the gas phase.

When we take r_0 = 2 cm, representative of an actual, small reaction vessel, then the above formula yields $t \simeq 1000$ s. This is a sufficiently long time that O_3 addition reactions to olefins can usually be taken as nearly adiabatic. The reaction under usual conditions is so fast that it is essentially diffusion controlled or else mixing controlled. A dilute 0.1 M olefin solution reacting with O_3/O_2 gas mixture has an exothermicity of some 55 kcal/mol and would liberate about 5.5 cal/cm^3 soln. For ρc_v ~0.3 cal/cm^3·°C the adiabatic temperature rise would be about 18 °C. More concentrated solutions would liberate proportionately more heat. As we shall note later, the isomerization to final products, the stable ozonide, is equally exothermic. Thus, if the reaction is run at $T \geq 210$ K, where the subsequent isomerization becomes rapid, $\Delta T_{\text{adiab}} \geq 36$ °C and the well-known explosive hazards of working with ozonation are quantitatively documented. Equally noteworthy also is the difficulty of monitoring reliable temperature control in ozonation. This probably accounts for some of the discordant kinetic data which have been reported.

That the addition does occur in a concerted manner is further supported by the experimental results obtained from the ozone reaction with trans isomers of 2-butene, 2-pentene, and 3-hexene[26] wherein the α-diols obtained by reduction of the corresponding molozonides with isopropyl Grignard reagent at −115 °C in ether solution were what one would expect from the cis addition of O_3 to the olefinic double bond. Also NMR spectra of the molozonides from the cis and trans alkenes showed that the methine absorptions of the two molozonides stereoisomers were quite different.[26c,27]

Decomposition of the Primary Ozonide

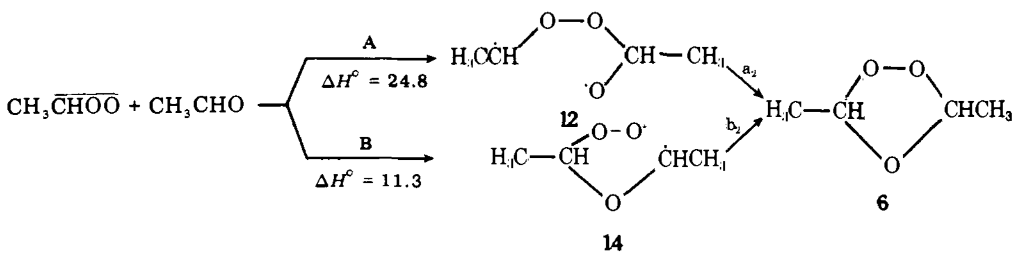
Stable ozonides have the general structure of a five-membered ring (1,2,4-trioxolane).[9,12] The transformation from the primary ozonide to stable ozonide is very rapid above 210 K($\tau \simeq 10$) and is believed to proceed via a very reactive carbonyl oxide. Using the data of Table I for a hypothetical biradical path (eq III) the initial step can be estimated to be endothermic by 17 kcal. The overall change from ozonide to the zwitterion plus aldehyde is estimated to be exothermic ($\Delta H° = -2.7$ kcal) for a value of the stabilization energy Δ equal to 22 kcal/mol. The biradical intermediate formation process (eq III) would be extremely slow (even assuming a high A factor $\sim 10^{15.7}$ s^{-1} as is found in peroxide decompositions) at low temperatures such as −130 °C where primary cis ozonides have been found to be unstable. It is thus ruled out. Supporting this conclusion, a transition-state calculation indicates that the A factor for this bond fission is $\leq 10^{14.5}$ s^{-1}, making the radical path still slower. The remaining possibility is the concerted decomposition path, which as shown above is exothermic. If we make use of the value of activation energy, 12.5 kcal/mol, deduced[6] from the data for *trans*-3-hexene[26c] and lower it by 1 kcal/mol for the cis olefin because of steric interactions, we find that the half-life turns out to be over 1 h at 150 K if $A = 10^{13}$ s^{-1}. In order to be able to monitor any change within a reasonable time, as has been done by Bailey et al. using NMR,[28] would require a faster decomposition. Since the molozonides were prepared at −155 °C and found to be stable, the excess energy resulting from the exothermicity of their formation ($\Delta H° \sim -58$ kcal/mol) must be dissipated to the surrounding media as already noted. Thus the activation energy must be still lower. A lowering of 0.5 kcal/mol to 12 kcal at 150 K would decrease the half-life to ~14 min compatible with the observations. We therefore conclude that the intermediate step leading to formation of the reactive carbonyl oxide is also a concerted process. The existence of these oxides has been inferred from the observed structures of the stable ozonides, which include mixed ozonides when new aldehydes R″CHO are added to the mixture to compete with the olefin-produced aldehyde RCHO (or R′CHO from R′CH=CHR) and finally from the chemical trapping of R′CHOO with alcohols at low temperature.[29,30] We shall review this last feature later.



(III)

Addition of Carbonyl Oxides to Aldehydes

The recombination of aldehyde and carbonyl oxide to form stable ozonide has been found to be extremely rapid. In early experiments at chemical trapping, Criegee failed to find mixed ozonides when "foreign" aldehydes were added to the reaction mixture and this led him to conclude that the recombination was entirely cage controlled.[31] As we shall see, this is not entirely correct. We can picture the reaction as proceeding via two distinct paths, one biradical and one concerted. The biradical path may itself take either of two isomeric channels. Continuing with our example of 2-butene + ozone we write eq IV. As is shown in IV both processes, A and B, leading to the biradical formation are endothermic, the former by 25 kcal/mol and the latter by 11 kcal/mol (Table I). The concerted

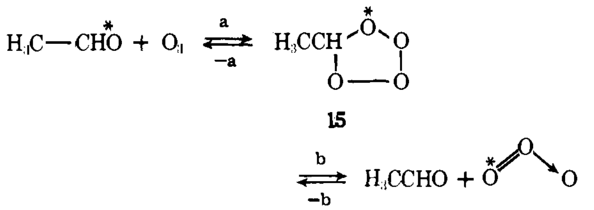

(IV)

production of ozonide is, however, exothermic to the extent of 53 kcal/mol for the chosen value of Δ = 22 kcal/mol. Biradical formation could not occur even at ambient temperatures with any significant rate but the concerted process would occur. It thus turns out that all three steps in the Criegee mechanism must occur in a concerted fashion. It should be noted that the ion pairs corresponding to structures **12** and **14** are more stable at r_{ip} = 2.6 Å by 10.0 kcal + ΔH_{solv}. The latter could make both exothermic in polar solvents (see the discussion later on).

O-Atom Exchange of Aldehydes with Ozone

Murray, Story, and their collaborators[32] concluded from the observed cis-trans ratios of cross-ozonides obtained from the ozonolysis of unsymmetrical olefins and which were correlated with olefin geometry that a new aldehyde exchange mechanism was operative. This fitted very well with the stereoselectivity observed in the ozonolysis reactions and also explained the incorporation of ^{18}O atoms, present in the "foreign" aldehyde, in the peroxide bridge as deduced from the mass-spectral fragmentation patterns obtained from the ozonides.[33] However, subsequent work by Higley and Murray[34] in which they used triphenylphosphine for reduction of the ozonide containing ^{18}O atom has shown that the latter atom is exclusively incorporated in the ether position as required by the Criegee mechanism. This kind of observation would exclude any nonzwitterionic path for the formation of ozonides (in this particular case). Klopman and Joiner[35] have attempted, however, to explain the incorporation of ^{18}O from the aldehyde in the peroxy bridge on the Criegee model. We shall show that this is unlikely from thermochemical considerations.

If O-atom labeled aldehyde (RCHO*) does not enter the peroxide bridge of the ozonide, we must seek other routes for an artifact leading to such incorporation. One route is a direct exchange between aldehyde and ozone. The mechanism would have to be (V). Neglecting isotope effects, $k_{-a} = k_b$ and $k_{-b} = \frac{1}{2}k_a$. The formation of cyclic tetraoxide **15** is endothermic by 5.6 kcal/mol (Table I) and, if we further assume an intrinsic activation energy of 5.0 kcal/mol, the amount observed for highly exothermic molozonide formation, we estimate a minimum 10.6 kcal/mol activation energy for the step a. As step a is stipulated to be a concerted one like O_3 addition to olefins, the A factor for this process would be $10^{6.5}$ M^{-1} s^{-1}, which would make k_a (M^{-1} s^{-1}) = $10^{-4.9}$ at 200 K and $10^{-1.4}$ at 300 K. The former value is much too small to produce exchange at 200 K in agreement with the recent observations,[34] while the latter is too small relative to the estimated rate of O_3-olefin reactions at 300 K to be a significant source of exchange ($\leq$0.01%) in the final ozonide. On the other hand, it is compatible with the appreciable exchange observed at 300 K between O_3 and isobutyraldehyde[35] in heptane solution.


(V)

Stereochemical Considerations

Many of the experimental efforts to understand the mechanism of ozonolysis have been linked to the determination of cis/trans ratios of the ozonides that are obtained from the stereoisomers of the alkenes, both symmetrical and unsymmetrical. The simple Criegee model predicts this ratio as unity, contrary to experimental data, which provides evidence for small changes in this ratio with (a) the solvent, whether polar or nonpolar, (b) the warm-up rate of the ozonolysis mixture, (c) the temperature of the ozonolysis, and (d) the effect of added aldehyde. It was the cis/trans ratios of the cross-ozonides obtained from unsymmetrical olefins that led Story, Murray, and co-workers to propose the model of aldehyde exchange.[32,33] Bailey et al.,[36] on the other hand, formulated three principles to modify the Criegee mechanism so as to explain the small, observed stereochemical selectivity in the ozonide formation. They involve the basic concept of the geometry of the zwitterion, whether syn or anti, along with their interconvertibility. The rationale for these rules is traced to the principle of least motion.[37] Bailey[12] has discussed the role of various above-mentioned parameters in influencing the ozonolysis products and the mechanistic considerations to be taken into account from such products.

We have examined the original data on the production of cross-ozonide from mixtures of pairs of olefins[38] (3-hexene with 3-heptene, etc.) with ozone at −70 °C or of mixtures of olefins and aldehydes with ozone at −70 °C and find that the yields of crossed ozonides can be fitted very well to a model in which one has about 60% of cage recombination of the nascent aldehyde and carbonyl oxide species. This raises some interesting questions about the concerted process for aldehyde-carbonyl oxide addition which we have seen must have a relatively low Arrhenius A factor of about $10^{6.5}$ M^{-1} s^{-1} [39] at $T > -100$ °C where the primary ozonides are unstable. The activation energy for cage escape must exceed aldehyde addition by about 2.5 kcal for the two to be competitive. This is compatible with a dipole-dipole attraction between aldehyde and carbonyl oxide of about 5 kcal,[40] which seems reasonable, and would then place an upper limit of about 2-3 kcal/mol on the activation energy for the concerted addition of carbonyl oxide to aldehyde. This latter also seems reasonable by comparison with the activation of 2-5 kcal/mol observed for the equally exothermic addition of O_3 to the much less polar olefins.

Deviations in the cis/trans ratios from unity are of the order of 10-50% corresponding to values from 0.67 to 1.5. Such small deviations in turn reflect free-energy differences of $\leq$0.2 kcal/mol at 200 K. While the Bauld-Bailey rules may be very useful in accounting for the trends observed, we are unable to make any fruitful thermochemical analysis of them at the present state of the art. Such variations are well within the range of solvent interactions even in nonpolar solvents.

Reaction of Ozone with Saturated Compounds

Ozone has been found to react rapidly with alcohols and ethers even at −78 °C.[41] About 40 years ago Durland and Adkins[42] reported the stereospecific oxidation of decalin (both *cis-* and *trans-*) to the corresponding 9-decanol. Whiting et al.[41] later found that the reaction proceeds even at −78 °C and reported also that adamantane at −78 °C is slowly oxidized to the 1-alcohol and ketone in the ratio of 3:1. They further found that CH_3OH reacts at −78 °C with O_3 in $CFCl_3$ solutions with a half-life of minutes while 2-propanol is much faster. The products from MeOH + O_3 when examined (after warming to 0 °C) were about 85% ($HCOOH + H_2O_2$) and about 15% ($CH_2O + O_2$). Ethanol gave about 70% ($CH_3COOH + H_2O_2$) with about 27% (CH_3CHO) and 2% of ($CH_2O + CH_3CO_3H$). About 18% of O_2 was evolved.

Hamilton et al.[43] reported the initial products of O_3 + cyclohexane as cyclohexanol and cyclohexanone in a ratio of about 3.5:1. Bailey et al.[44] studied amine oxidation in $CHCl_3$ solutions (down to −60 °C) and found quantitative yields of products. From t-$BuNH_2$ they found about 60% t-$BuNH_3Cl$ and about 18% each of t-$BuNO_2$ and t-BuNCO.

It was earlier postulated that hydrotrioxides, RO_3H, were very likely the unstable intermediates in the ozonolysis of various organic substrates. However, only recently has spectroscopic evidence for their existence (prior to Plesničar et al.) become available.[45] In recent studies, Plesničar et al.[46,47] reported the formation of stable acetal hydrotrioxides at $T \leq -50$ °C obtained by reacting acetals with O_3. The authors also studied the kinetics of their decomposition from −40 to −10 °C, both in neat form and dissolved in selected solvents. Another recent study by Pryor et al.[48] describes the kinetics of ozonation of *tert*-butyl hydroperoxide in a number of solvents at temperatures between −60 and +20 °C.

Mechanism of Ozonation of Saturates

The unusual reactivity of O_3 at low temperatures suggests a radical pathway for its behavior. This can take either of two paths, a chain reaction initiated by O atoms formed from the reversible dissociation of O_3

$$O_3 \rightleftharpoons O_2 + O \ (\Delta H = 24 \text{ kcal/mol}) \qquad (VI)$$

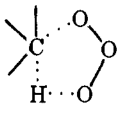
or a H-atom abstraction reaction followed by cage recombination of fragments:

$$O_3 + RH \underset{-a}{\overset{a}{\rightleftarrows}} [R\cdot + HO_3\cdot] \xrightarrow{b} RO_3H \qquad (VII)$$

The chain reaction (VI) can be easily discounted. Under usual conditions, the fastest reaction of O atoms will be the reverse combination with O_2 which in solution should be close to the diffusion-controlled limit.[49] Competing reactions with O_3 have $E_{act} \sim 4.5$ kcal and with saturates $E_{act} \sim 4$-7 kcal/mol.[50] While the latter reactions with saturates might be fast enough to support a chain in concentrated solutions (>0.1 M), the products would be alcohols and water, not trioxides, and the rates would be prohibitively slow at −78 °C.[51]

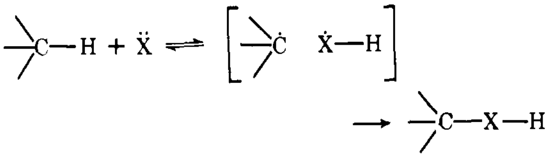
The atom abstraction path (VII) had been earlier discounted as being too endothermic at −78 °C.[41,52] With the new $\Delta H_f°(HO_3\cdot)$, however (Table I), the H-O_3 bond strength is now raised to 68.5 kcal. This would lead to measurable attack on RH at 300 K if the R-H bond strength were not in excess of 87 kcal, which would exclude all the substrates described. At −78 °C, no measurable reaction is possible except for R-H bond strengths less than 80 kcal, again much lower than the bond strengths in the compounds discussed. Hence we affirm the earlier conclusions that the reaction cannot follow a radical pathway. If free-radical pathways are not available, then only concerted or ionic reaction mechanisms are left as possibilities.

The concerted reaction would amount to insertion into the C-H bond. The transition state for this reaction would be a five-membered ring



with a pentavalent carbon atom. The activation energy for this can only be crudely estimated but it turns out to be prohibitive. It has been estimated that the intrinsic activation energy for pentavalent carbon formation[53] is about 15-20 kcal, while there is an estimated additional 6 kcal for ring strain yielding a minimum expected value of 20-26 kcal. If we use an A factor of $10^{6.5}$ M^{-1} s^{-1} for the concerted process, then the maximum activation energy which can be accommodated to the observed rates is 8 kcal. An insertion path is thus also ruled out.

In actual fact there are no true examples of insertion reactions into a σ C-H bond. The very rapid reactions which have been observed for the apparent insertion of such excited species as $^1CH_2$ and O(^{1}D) into C-H bonds are more readily interpreted as abstractions followed by insertions.[54-56] Thus for the biradical $\ddot{X}$



(VIII)

When $\ddot{X}$ is in a singlet state, the abstraction reaction is quite exothermic and the radical pair (bracketed in eq VIII) is produced in a singlet state at a sufficiently small separation ($<3r°_{C\text{-}X}$) that recombination proceeds with unit efficiency.[54] We are thus left with the heterolytic pathway as the mechanism for O_3 reaction with saturated compounds.

Thermochemistry of Ionic Reactions

The heterolytic reaction path for O_3 could conceivably follow either of a number of routes. It could take place by electron transfer from RH to produce the ion pair:

$$RH + O_3 \rightleftharpoons [RH^+ \cdots O_3^-] \qquad (IX)$$

It could also take place via proton transfer:

$$RH + O_3 \rightleftharpoons [R^- \cdots HO_3^+] \qquad (X)$$

Or finally, it could occur by hydride ion transfer:

$$RH + O_3 \rightleftharpoons [R^+ \cdots HO_3^-] \qquad (XI)$$

While mechanistically we can visualize a smooth transition from the ion pairs shown in eq X and XI to RO_3H, it is very difficult to see how the ion pair of eq IX could form such a product.

If we know the electron affinities (EA) and ionization potentials (IP) of the various species involved together with the associated bond strengths (DH°), we can calculate the energy required to form the ion pairs at infinite separation in vacuo, $\Delta E_{ip(\infty)}$. For eq IX, for example,

$$\Delta E°_{ip(\infty)} = IP(RH) - EA(O_3) \qquad (XII)$$

while for eq X

$$\Delta E°_{ip(\infty)} = DH°(R\text{-}H) - DH°(\dot{O}_3\text{-}H) + IP(R\cdot) - EA(HO_3\cdot) \qquad (XIII)$$

When the ion pair is formed at a distance r_{ip} separating the effective charge centers, $E°_{ip(\infty)}$ is reduced by the Coulombic energy of attraction (ϵ^2/r_{ip}) of the unit charges:[57]

$$\Delta E°_{ip(r)} = \Delta E°_{ip(\infty)} - \epsilon^2/r_{ip} \qquad (XIV)$$

Finally, when the ion pair is formed in a solution, we must reduce the energy still further by ΔE_{solv}, the differences in solvation energies of the ion pair and the reactant molecules:

$$\Delta E_{ip(r)}(\text{solvent}) = \Delta E°_{ip(\infty)} - \epsilon^2/r_{ip} - \Delta E_{solv} \qquad (XV)$$

Values for the bond strengths are known for almost all the species of interest to ±1 kcal,[3,4] as are the electron affinities and ionization potentials of the molecules and radicals,[13,14] but

Table II. Ionization Potentials and Electron Affinities of Some Radicals and Molecules[a]

species	electron affinity, eV	species	ionization potential, eV
H	0.77	C_2H_5	8.35
CH_3	~0.1	allyl	3.2
C_2H_5	~0.3	*i*-Pr	7.5
O	1.46	c-C_6H_{11}	7.40
O_2	0.44	*t*-Bu	6.9 (6.7)
O_3	2.2	*sec*-Bu	7.62
OH	1.83	HO	13.2
HO_2	1.85	HO_2	11.5
HO_3	1.85	CH_3O	8.3 ± 0.2
CH_3O	1.57	CH_2OH	7.42
n-PrO	1.9	CH_3CHOH	6.85
SH	2.2	O_2	12.0
		t-BuO_2	6.75
		C_2H_6	11.5
		cyclohexane	9.8
		i-C_4H_{10}	10.6

[a] Data taken from ref 13, 14, and 15b.

with somewhat less accuracy, perhaps ±2.5 kcal. The Coulombic energy of the ion pair depends only on the charge separation, r_{ip}, and this is about 2.8 Å for ions pairs of the light elements in the periodic table (atomic numbers 3 to 12)[58] when measured in ionic crystals. Ion pairs in the gas phase, however, seem to be contracted by about 15% to 2.4 Å, an effect which has been attributed to the enhancement of repulsive forces in the crystal. We will choose a mean value of 2.65 ± 0.05 Å for r_{ip} of the ion pairs in solvents, which gives the Coulombic term $\epsilon^2/r_{ip} = 5.4 \pm 0.1$ eV. In Table II we list the values of IP and EA for the molecules and radicals of interest here.

The energy of solvation of ion pairs with which we shall be concerned can be estimated in two different ways. Kirkwood[59] has derived a formula for the Gibbs free energy of solvation, $\Delta G_D°$, of a spherical (radius R_c) point dipole μ, immersed in a structureless classical solvent of dielectric constant D:

$$\Delta G_D° = -\frac{\mu^2(D-1)}{R_c^3(2D+1)} \qquad \text{(XVI)}$$

Solvation of the dipole entails loss of entropy and is calculable from $\Delta G_D°$. On differentiating with respect to temperature, we obtain the following expression for the entropy of solvation, $\Delta S_D°$:

$$\Delta S_D° \equiv -\left(\frac{\partial \Delta G_D°}{T}\right)_P = \frac{-\Delta G_D°}{T}\left[\frac{3D}{(2D+1)(D-1)}\left(\frac{\partial \ln D}{\partial \ln T}\right)_P\right] \qquad \text{(XVII)}$$

On subtraction we obtain the enthalpy of solvation, $\Delta H_D°$:

$$\Delta H_D° = \Delta G_D° + T\Delta S_D° = \Delta G_D°\left\{1 + \frac{3D}{(2D+1)(D-1)}\left|\frac{\partial \ln D}{\partial \ln T}\right|\right\}_P \qquad \text{(XVIII)}$$

$$\simeq [1.1 \pm 0.08](\Delta G_D°) \qquad \text{(XIX)}$$

The empirical result (eq XIX) derives from the fact that for the usual solvent of interest here the term in parentheses in eq XVIII stays within fairly narrow limits as shown.

If we choose μ(ion pair) = $\epsilon \times 2.65$ Å = 12.72 D and R_c = 3.5 Å, then

$$\Delta G_D = -27.2(D-1)/(D+1/2)\ \text{kcal/mol} \qquad \text{(XX)}$$

$$\Delta H_D \sim -30(D-1)/(D+1/2)\ \text{kcal/mol}$$

At $D = 2$, typical of hydrocarbon solvents, these values become $\Delta G_D = -11$ and $\Delta H_D = -12$ kcal/mol. At $D = 10$ they are about −23 and −25 kcal/mol, respectively, very close to their limiting values. Corresponding values of ΔS_D are always negative and range from about −8 to −15 cal/mol·K depending on the solvent. We shall employ a mean value of −11 ± 4 cal/mol·K for $\Delta S_D°$.

The Kirkwood formula gives a minimum value for $\Delta G_D°$ of ion-pair solvation. The idealization of a point dipole instead of an extended charge dipole with extension comparable to solvent separation underestimates the field in the immediate neighborhood of the ion pair from 10 to 40% with a corresponding error in the energy for solvents of dipole moment >1.0 D. For low dielectric constant solvents with small dipole moment, the near field error leads to an error of about 20–80% in the much lower first-shell energy. We have constructed discrete models using van der Waals radii and no more than four solvent molecules. We have found for these the deviations from the Kirkwood formula described above. Because we are still engaged in these discrete model calculations we shall continue to employ the Kirkwood model, understanding that solvation energies may be underestimated by as much as 25%.

Ozonation of Hydrocarbons

We can now consider the hypothetical oxidation of pure liquid C_2H_6 at −80 °C by O_3. Using the preceding formula and the data on bond dissociation energies and other data from Tables I and II we find for the process:

$$C_2H_6(l) + O_3(l) \rightleftharpoons [C_2H_5^+ \cdots HO_3^-] \qquad \text{(XXI)}$$

$$\Delta H°_{ip(r)}[C_2H_6(l)] \simeq 44\ \text{kcal/mol}$$

This process is so endothermic that no solvation energy could come close to compensating the unfavorable combination of ionization potentials and bond energies.

By way of contrast, the similar reaction for liquid i-C_4H_{10} yields the value

$$i\text{-}C_4H_{10}(l) + O_3(l) \rightleftharpoons [t\text{-}C_4H_9^+ \cdots HO_3^-] \qquad \text{(XXII)}$$

$$\Delta H_{ip(r)}[i\text{-}C_4H_{10}(l)] \simeq 2\ \text{kcal/mol}$$

The lower IP (*t*-Bu) compared to IP(Et) (Table II) has changed the endothermicity so much that, even with the minimum solvation enthalpy, the endothermicity is sufficiently low that reaction XXII becomes the most attractive path for the low-temperature reaction.

We can take cyclohexane ozonation as typical of the secondary CH_2 group. The initial products are cyclohexanol and cyclohexane in an estimated ratio of 3.5:1.[43] We shall show that the hydrotrioxide is most likely to be the initial product formed by the ion-pair route and is subsequently followed by the radical decomposition of the hydrotrioxide to alcohol and ketone. For the initial step:

$$c\text{-}C_6H_{12} + O_3 \rightleftharpoons [c\text{-}C_6H_{11}^+ \cdots O_3H^-] \qquad \text{(XXIII)}$$

$$\Delta H_{ip(r)}[c\text{-}C_6H_{12}(l)] \simeq 20\ \text{kcal/mol}$$

With an A factor of $10^{7.5}$ L/mol·s, estimated by using $10^{9.2}$ for the radical reaction[4] and $\Delta S_{ip}° \simeq -8$ eu, the overall rate constant for the ion-pair formation is given by

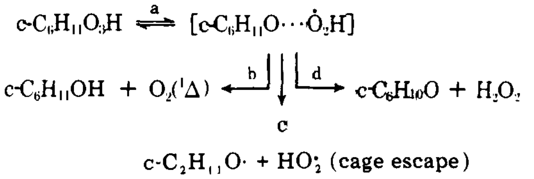
$$k_{ip}(\text{XXII}) \simeq 10^{7.5-18/\theta}\ \text{L/mol·s}$$

At 25 °C this would predict a half-life for O_3 in neat cyclohexane of about 2 days. A reduction of E to 17 kcal, which is well within the combined uncertainties of $\Delta H°_{ip(r)}$, would fit the observed reactivity.[10]

We have discussed elsewhere the decomposition of alkyl trioxides of the general formula RO_3R' where R′ is either an alkyl group or H atom.[8,60] The weakest bond has a dissociation energy of 22.5 kcal/mol (RO_2–OR or RO–O_2H) and an estimated A factor of $10^{16}\ \mathrm{s}^{-1}$. These compounds should decompose appreciably rapidly above −40 °C in agreement with observations we shall discuss shortly. In the preceding abstraction reaction to form an ion pair, one would expect the equatorial H atom in cyclohexane to be the most accessible. The tight interaction between the two ions together with strong solvation would tend to maintain this conformation, in agreement with stereochemical observations.[10] Thus one would expect to see equatorial hydrotrioxide products. In the case of methylcyclohexanes, the stable configurations would favor attack on the axial tertiary H atom. On the other hand, the difference of only 1.6 kcal between axial and equatorial methyl would still permit a kinetically favored attack on the axially unfavorable conformation. It is difficult to distinguish such stereochemical direction from slow conformational reorientation in the caged ion pair.

Whiting[3] reported from 80 to 90% retention of configuration in the ozonation of *cis-* and *trans*-dimethylcyclohexanes and even higher values for *cis-* and *trans*-decalins.[41,42] This would suggest a difference of about 1.5 ± 0.6 kcal/mol in the reaction pathways leading to the two possible geometries, quite consistent with the solvation barriers which might be estimated for the ion-pair rotation required to produce an inverted geometry in the solvent cage.

The radical decomposition would produce a singlet caged radical pair which could disproportionate in either of two directions:



$$\text{c-C}_6\text{H}_{11}\text{O}_3\text{H} \overset{a}{\rightleftharpoons} [\text{c-C}_6\text{H}_{11}\text{O}\cdots\dot{\text{O}}_2\text{H}]$$

$$\text{c-C}_6\text{H}_{11}\text{OH} + \text{O}_2(^1\Delta) \xleftarrow{b} \quad \xrightarrow{d} \text{c-C}_6\text{H}_{10}\text{O} + \text{H}_2\text{O}_2 \qquad \text{(XXIV)}$$

$$\downarrow \text{c}$$

$$\text{c-C}_2\text{H}_{11}\text{O}\cdot + \text{HO}_2^{\cdot}\ \text{(cage escape)}$$

Note that the nascent radical pair is formed in a singlet state so that the disproportionation will produce singlet O_2 (eq. XXIV, b) or singlet ketone (path d). As we shall discuss later the radicals which escape the cage can initiate a chain reaction. Both disproportionation paths, b and d, are very exothermic, by 55 and 75.5 kcal/mol, respectively,[4] so that the products will be formed with large excitation energies.

Ozonation of Alcohols

Methanol is the slowest of the alcohols to react with O_3 at −78 °C in Freons ($CFCl_3$ with D = 2.3).[41] Using the data on bond strengths[4] together with that in Tables I and II we estimate for the ion-pair process

$$CH_3OH + O_3 \rightleftharpoons [HOCH_2^+\cdots HO_3^-] \qquad \text{(XXV)}$$

$$\Delta H_{\mathrm{ip}(r)}[CFCl_3\,(l)] \simeq 15.2\ \mathrm{kcal}$$

$$\Delta H_{\mathrm{ip}(r)}[CH_3OH(l)] \simeq 1.2\ \mathrm{kcal}$$

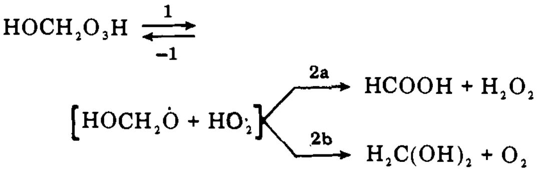
The Freon solvent with a relatively low dielectric constant (D = 2.3) would lead to a bimolecular rate constant:

$$k(\mathrm{XXV},CFCl_3) \sim 10^{7.2-15.2/\theta}\ \mathrm{L/mol{\cdot}s}$$

while the alcohol as solvent (with D = 45 at 200 K) would have an activation energy lower by some 14 kcal. At 200 K, O_3 would have a half-life immeasurably long in $CFCl_3$ (~0.1 M CH_3OH), while it would be immeasurably short (~10^{-6} s) in pure alcohol. The observed qualitative observations[41] suggest a half-life of about 10^3 s in ~0.1 M solution, which would require an activation energy of about 9.0 ± 0.5 kcal/mol. If in fact the alcohol is present predominantly as trimers at −200 K at the 0.1 M concentrations used,[62] then there will be two or more other alcohols in the solvent cage with the ion pair and the effective solvation energy contributed will easily lower the activation energy by some 6 kcal/mol or more.

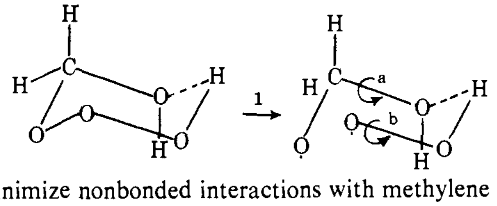
As we go to CH_3CH_2OH with a secondary CH_2 group, with 3 kcal/mol lower C–H bond strength and an ionization potential for the radical $CH_3\dot{C}HOH$ lower than $\dot{C}H_2OH$ by some 0.2–0.4 eV (4.5–9.0 kcal/mol), we expect an activation energy below 6 kcal/mol and an appropriately fast rate of reaction with O_3 as reported.[41] For isopropyl alcohol the same type of calculation yields an activation energy for ion-pair formation of about 1 kcal/mol even in very dilute $CFCl_3$ and an immeasurably fast rate at −78 °C also as reported.[10]

The decomposition of the resulting hydroxymethyl hydrotrioxides should follow the same radical paths indicated for the alkyl hydrotrioxides (eq XXIV) with essentially the same rate constants, again in agreement with the qualitative observations reported. Taking the methanol derivative as an example



$$\mathrm{HOCH_2O_3H} \underset{-1}{\overset{1}{\rightleftharpoons}} [\mathrm{HOCH_2\dot{O} + HO_2^{\cdot}}] \begin{cases} \xrightarrow{2a} \mathrm{HCOOH + H_2O_2} \\ \xrightarrow{2b} \mathrm{H_2C(OH)_2 + O_2} \end{cases} \qquad \text{(XXVI)}$$

With k_{2a}/k_{2b} ~6 the product yields are properly accounted for.[10] Structural considerations of the hydrotrioxide show that the molecule can exist in a six-membered cyclic form wherein the hydrotrioxidic H atom is H bonded to the alcoholic O atom and the alcoholic H atom is axial to the cyclic structure to minimize nonbonded interactions with methylene hydrogens. Alternatively the alcoholic OH bond may replace the peroxidic OH in the ring. The fragments formed in the cage (still hydrogen bonded) can either diffuse out of the cage or undergo rotations, either around C–O bond (a) or around O–O (b). Rotation a through ~100° brings the axial methylene hydrogen into bonding distance of the O atom of the HO_2 species and can yield the observed major products. Rotation b would involve a somewhat higher energy due to the existence of H bonding and would be less likely unless the H bonding were reversed. It would lead to the main products via step 2b. If step −1 were fast compared to (2a) or (2b), the minimum rate of reaction would be given by $k_{\mathrm{exp}} = K_1k_{2a}$ where K_1 is the equilibrium constant for radical pair formation in the solvent cage ($\Delta S_1° \sim 20$ eu; $\Delta H_1° \sim 23$ kcal/mol).[4,5] If k_{2a} is rotation controlled and equal to $10^{11.5-1/\theta}\ \mathrm{s}^{-1}$,[4] we find $k_{\mathrm{exp}} \sim 10^{16-(24/\theta)}\ \mathrm{s}^{-1}$. Under these conditions $k_{\mathrm{exp}} \sim 10^{-3.0}\ \mathrm{s}^{-1}$ at 273 K. On the assumption that there was 100% conversion of O_3 into hydrotrioxide, the latter's concentration would be 65 μmol/cm³, whence the rate of formation of H_2O_2 turns out to be ~200 μmol/cm³·h, which is faster than the observed value of 50 μmol/cm³·h but suitably close, considering the combined uncertainties of estimation.

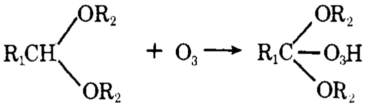


(XXVII)

For ethanol the major products from the ozonation and subsequent decomposition of the hydrotrioxide were about 60% $CH_3COOH + H_2O_2$ in nearly equimolar quantities[10] with lesser amounts (~30%) of $O_2 + H_2O$ + acetaldehyde, parallel to the methanol reaction. Whiting[10] suggested a base-catalyzed decomposition to account for the major products. It is unlikely that any of the plausible bases such as CH_3OH would attack the C–H hydrogen atom, however. They are much more likely to bond to the polar HO bonds at the hydroxy or peroxy end of the molecule. Attack here would have an unacceptably high activation energy if heterolytic and would not account for the minor products. In view of the well-documented and energetically acceptable unimolecular radical path, the catalytic path is not really needed.

Thermal Decomposition of Acetal Hydrotrioxides

Plesničar et al.[46,47] have reported the formation of stable acetal hydrotrioxides (VIII) by the reaction of O_3 with acetals (VII) and characterized them using NMR spectroscopy. The kinetics of their decomposition were studied either with the neat materials or diluted with solvent such as Et_2O or CH_2Cl_2. The reported Arrhenius parameters for observed first-order kinetics have limited accuracy since the temperature interval of investigation for each kinetic study was 10-30 °C. For an error of ±0.5 °C in the temperature measure, the reported value of activation energy would be uncertain by ±10%. For dimethyl acetal hydrotrioxide (VIIIa) they reported $\log k_a\ (s^{-1}) = 11.8 - 16.1/\theta$, while for diethyl compound VIIIb $\log k_b\ (s^{-1}) = 11.1 - 14.5/\theta$ at the two temperatures, 253 and 263 K; for the compound VIIIc the reported $\log k_c = 15.8 - 19.0/\theta$ and for VIIId $\log k_d\ (s^{-1}) = 12.2 - 14.9/\theta$, where the two temperatures of investigation were 233 and 243 K. While the low A factors observed for VIIIa, VIIIb, and VIIId are indicative of chain reactions, the higher value for VIIIc makes these conclusions somewhat tenuous owing to the limited accuracy in activation energies as noted above. The authors while proposing the existence of both radical and nonradical paths for the decompositions presented a radical mechanism to explain the products of decomposition. In the case of diethyl acetal hydrotrioxide (VIIIb) these were ethyl acetate (0.80-0.85 mol/mol of O_3 absorbed), ethanol (0.7-0.75 mol) and water, acetaldehyde, acetic acid, ethyl formate, diethyl carbonate, and small amounts of gases presumed to be methane and ethane. They also reported the presence of two peroxides not completely characterized but probably alkyl hydroperoxide and dialkyl peroxide. Small amounts of H_2O_2 were also detected. An important product of decomposition of the hydrotrioxides was the singlet O_2, whose reported yield (relative to O_3 absorbed) varied with the parent substrate, in the range 45-80%. These must be considered as minimum values because of loss of singlet O_2 by quenching.



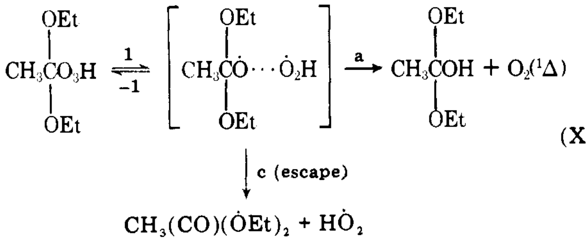
$$R_1CH(OR_2)_2 + O_3 \longrightarrow R_1C(OR_2)_2{-}O_3H \qquad \text{(XXVIII)}$$

VII VIII

a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = C_2H_5$
c, $R_1 = Ph$; $R_2 = \dot{C}H_3$
d, $R_1 = Ph$; $R_2 = \dot{C}H_2$

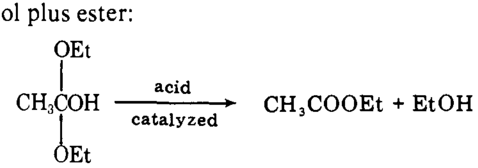
where both R_2's are interlinked

We would expect the rate constants for the acetals to be of the same order or slightly faster than that calculated for ethyl and isopropyl alcohols since the C-H bond strengths, ionization potentials of the resulting radicals, and the solvation energies will be comparable. The decomposition should then follow the same paths indicated for the other hydrotrioxide (eq XXIV and XXVI), producing a caged radical pair, $HO_2\cdot$ + alkoxy radical. With the acetals, however, cage disproportionation can only take one path, giving singlet O_2 + hydroxy acetal. Structure VIIIb is used as an example in (XXIX). We would conclude that cage products (path a) account for 50-80% of the products and that the chain can account for the remainder. Note that the hemiacetal will split, under the reaction conditions, into alcohol plus ester:



$$CH_3C(OEt)_2O_3H \underset{-1}{\overset{1}{\rightleftharpoons}} \left[CH_3C(OEt)_2\dot{O}\cdots\dot{O}_2H\right] \xrightarrow{a} CH_3C(OEt)_2OH + O_2(^1\Delta) \qquad \text{(XXIX)}$$

$$\left[CH_3C(OEt)_2\dot{O}\cdots\dot{O}_2H\right] \xrightarrow{c\ \text{(escape)}} CH_3(CO)(\dot{O}Et)_2 + H\dot{O}_2$$



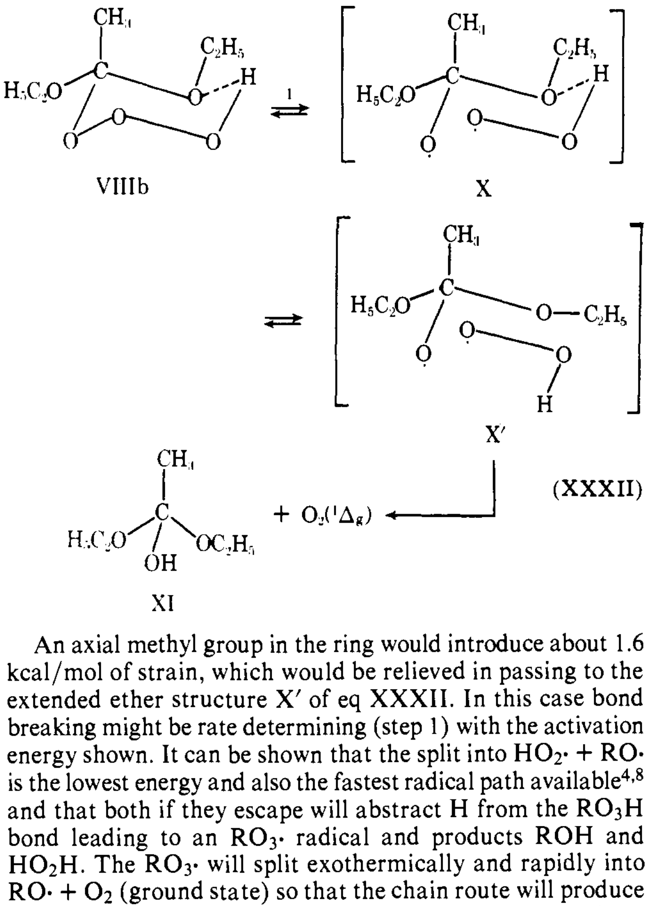
$$CH_3C(OEt)_2OH \xrightarrow[\text{catalyzed}]{\text{acid}} CH_3COOEt + EtOH \qquad \text{(XXX)}$$

Using the same Arrhenius parameters chosen for the other hydrotrioxides but lowering the activation energy by 3 kcal we estimate

$$k = 10^{16.0-21/\theta}\ s^{-1} \qquad \text{(XXXI)}$$

which at 263 K is only a factor of 3 lower than the value reported.[47] At 263 K this value corresponds to a half-life of about 7 s. The fast rate and the large exothermicity of the rearrangement (33 kcal) suggest appreciable temperature gradients in the system[39] as we have already noted in our earlier discussion of the reaction of O_3 with olefins.

The 3-kcal lowering of the activation energy for the acetal compounds compared to the other alkyl hydrotrioxides is based on structural considerations. It is quite likely that the OH is internally hydrogen bonded to one of the acetals in a loose six-membered ring with a reaction path as shown in (XXXII).

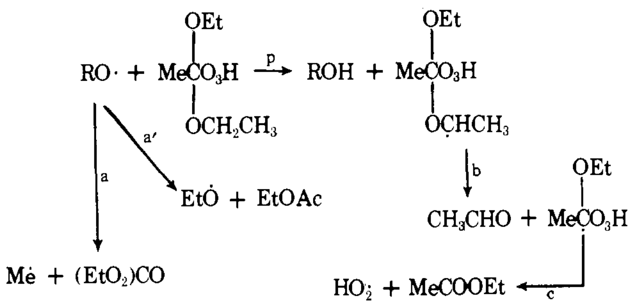


(XXXII)

An axial methyl group in the ring would introduce about 1.6 kcal/mol of strain, which would be relieved in passing to the extended ether structure X′ of eq XXXII. In this case bond breaking might be rate determining (step 1) with the activation energy shown. It can be shown that the split into $HO_2\cdot$ + $RO\cdot$ is the lowest energy and also the fastest radical path available[4,8] and that both if they escape will abstract H from the RO_3H bond leading to an $RO_3\cdot$ radical and products ROH and HO_2H. The $RO_3\cdot$ will split exothermically and rapidly into $RO\cdot$ + O_2 (ground state) so that the chain route will produce ROH + O_2 (ground state) predominantly. The main products may come from internal abstraction in $RO\cdot$ (expected to be slow), competing external abstraction from the CH_2 groups or unimolecular cleavage of RO (XXXII).

Both unimolecular cleavage paths a and a′ are slightly exothermic but may have activation energies of up to 8 kcal. This would make them faster than the bimolecular step p.

If we assume that initiation is by cage escape of radicals with efficiency $\alpha \leq 1$, propagation is by $RO\cdot$ radicals, and termination is by RO recombination, then a steady-state chain rate



(XXXIII)

is given by

$$-\frac{d(RO_3H)_{chain}}{dt} = k_p\left(\frac{k_i\alpha}{k_t}\right)^{1/2}(RO_3H)^{3/2} \quad (XXXIV)$$

where k_p may be estimated as $10^{8.0-2/\theta}$ L/mol·s for propagation, $k_t \sim 10^8$ for RO· recombination, and k_i is our bond breaking, $10^{16-22.5/\theta}$ s^{-1}.[5-7] The "apparent" unimolecular chain rate is then given by

$$k_{uni}(chain) \simeq k_p\left(\frac{k_i\alpha}{k_t}\right)^{1/2}(RO_3H)^{1/2} \quad (XXXV)$$

$$= 10^{12.0-13.3/\theta}\alpha^{1/2}(RO_3H)^{1/2}\ s^{-1}$$

Assigning $\alpha = 0.5$ and $RO_3H \sim 0.1$ M gives

$$k_{uni}(chain) \simeq 10^{11.3-13.3/\theta}\ s^{-1} \quad (XXXVI)$$

This is in excellent agreement with the absolute values reported for the rate constants.[46,47] Note that the cleavage paths a and a′ would not change these conclusions since propagation by EtO· radicals would have about the same properties as by RO·. The same is true of termination.

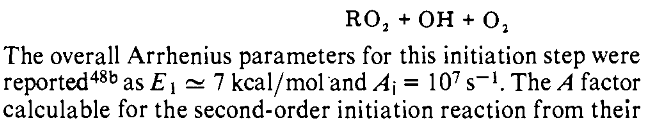
The chain mechanism, however, does not account for the minor products such as water, acetic acid, and ethyl formate.

Ozonation of Hydroperoxides

Kinetic studies of the ozonation of *tert*-butyl hydroperoxide have been reported by Pryor et al. The preliminary study[48a] reported the results of reaction carried out in $CFCl_3$ as a solvent in the temperature range −23 to +20 °C, though the major portion of the work involved only the temperature −4 °C. The subsequent detailed study[48b] was carried out in other solvents like CCl_4 and $CHCl_3$ and the temperature varied from −60 to −4 °C. The basic interpretation has remained unchanged. They suggested three mechanisms for the initiation step to generate t-$Bu\dot{O}_2$ radicals according to the following overall scheme where R = t=Bu:

$$ROOH + O_3 \xrightarrow{i} RO_2 + OH + O_2 \quad (XXXVII)$$

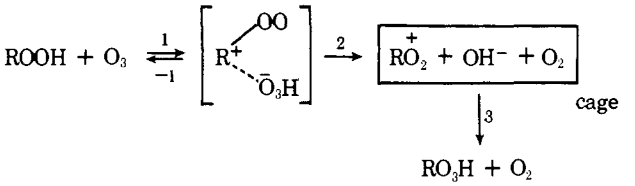
and on ground of energetics selected the so-called molecular-assisted homolysis (MAH) with the postulated transition state (TS) as



(XXXVIII)

The overall Arrhenius parameters for this initiation step were reported[48b] as $E_1 \simeq 7$ kcal/mol and $A_i = 10^7$ s^{-1}. The A factor calculable for the second-order initiation reaction from their data is found to be $10^{6.7}$ M^{-1} s^{-1}. The activation energy derived is about 50% of the estimated endothermicity in the initiation step. In order to account for the discrepancy, the authors have invoked the concept of a "molecular-assisted" process. From the latest data on $\Delta H_f°$, the heat of reaction of the initiation process, $\Delta H_i°$, = 10.8 kcal/mol instead of 14 kcal used by the authors. We believe that the explanation lies elsewhere. Their A factor, $10^{6.7}$ M^{-1} s^{-1}, is much lower than the normal values encountered for H-atom abstractions by radicals, which are in the neighborhood of 10^8–$10^{8.5}$ M s^{-1}. In this particular case, where an extra bond (O-O) is hypothesized to be weakened, the A factor should be still higher. An additional difficulty with the concerted MAH process is that it involves a change in spin. Excited, singlet O_2 would make the overall process more endothermic by 22 kcal. Singlet O_2 was looked for but not observed.

If it be postulated that O_3 abstracts a hydride ion (H^- ion) from the hydroperoxide to form the intimate ion pair (XXXIX), the energetics of the process can be calculated



(XXXIX)

following the same approach as before. Unfortunately, there seems to be a paucity of data on IPs of peroxy radicals. The only reported values are for n-pentyl- and n-heptylperoxy radicals, both in the neighborhood of 8.0 ± 0.2 eV.[14] We have estimated the value for *tert*-butylperoxy as equal to 6.75 ± 0.2 eV.[63] Since in the ion pair the center of positive charge would most likely be on the tertiary carbon of R (≡ t-Bu) and the negative charge on the terminal oxygen in HO_3^-, the distance of separation, r_{ip} in the ion pair can be taken as 2.80 Å, for which the Coulombic interaction energy is 5.15 eV. We then calculate for the energy of ion-pair formation (eq XXXIX)

$$\Delta H°_{ip(r)}[CFCl_3(l)] = 2 \pm 5\ \text{kcal/mol}$$

The recombination of the ion pair to form RO_5H is endothermic by 8 kcal/mol,[4] making the overall process from $RO_2H + O_3$ endothermic by about 10.5 kcal. A competing reaction is decomposition to HO^- and O_2 (ground state):

$$\begin{array}{lcccl} & HO_3^- \xrightarrow{\substack{\Delta H° = \\ -11.1\ \text{kcal}}} & OH^- & + O_2 & \text{(spin forbidden)} \\ H_f°(g) & (-22.6) & (-33.7) & (0) & (XL) \end{array}$$

It is exothermic by 11 kcal/mol. Enhanced solvation arising from the small size of HO^- compared to HO_3^- will increase the exothermicity of the process. In contrast, the spin-allowed path generating singlet $O_2(^1\Delta_g)$ will be endothermic by about 11 kcal at the maximum ($\Delta H_f° = 22.5$ kcal for $^1\Delta_g\ O_2$). Since evidence against the generation of singlet O_2 has been reportea by Pryor et al.,[48a,b] it is safe to conclude that it is the spin-forbidden process that occurs. Energetics for this process can be estimated by analogy with the similar decomposition reaction, $N_2O \rightarrow N_2 + O(^3P)$(spin forbidden). The observed activation energy for this latter process is close to the crossing point between the repulsive-state curve and the normal potential-energy curve, and is about midway between the endothermicities of the two types of processes. Adopting the same fraction, the estimated (minimum) activation energy (E_2) for the decomposition process

$$HO_3^- \xrightarrow{2} OH^- + O_2(^3\Sigma_g)$$

would be about one-half of 22.5 kcal = 11.5 kcal + ΔH(XL) = 0.4 kcal/mol with a relatively large uncertainty. On the basis of the postulated mechanism for initiation, the rate constant $k_i = K_1k_2$ where $K_1 = k_1/k_{-1}$, whence $E_i = \Delta H_1° + E_2 \simeq 3 \pm 6$ kcal, in plausible agreement with the value of ~7 kcal/mol reported by the authors for the initiation step. The mechanism proposed above differs from the one postulated by the authors only in the details of initiation.

The A factor for the hydride ion-pair process is estimated by our usual methods. For $\Delta S_1°$ we obtain (in liquid state) -29 eu, while $A_2 = (ekT/\bar{h}) = 10^{13.17}$ s^{-1}, giving for the A factor of K_1k_2 $10^{6.8}$ (M s)$^{-1}$, in excellent agreement with the reported value.[48]

Reaction of Carbonyl Oxides with Methanol

Some of the earliest evidence for the existence of carbonyl oxides came from scavenging reactions with CH_3OH.[29,30] When ozonolysis of secondary olefins was carried out in the presence of alcohols, or when methanol was added to the ozonolysis mixture at low temperatures before warm-up,[29] an almost quantitative production (based on O_3 used) of the geminal methoxy hydroperoxide $RCH(OCH_2)OOH$ was observed.

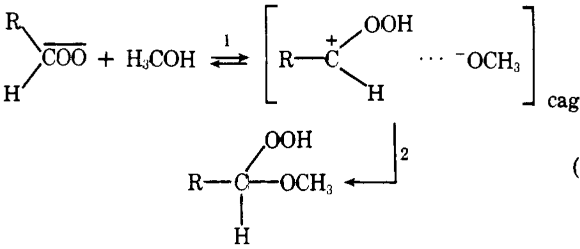
The formation of *gem*-methoxy hydroperoxide can be rationalized by an ionic pathway but not a radical one. In the biradical form of the zwitterion the abstraction of H atom from O-H in methanol (DH° = 104.0 kcal/mol) is endothermic by 37 kcal/mol (Table I) and this rate becomes insignificant at any temperature up to 1000 K. The abstraction from the weaker C-H bond is endothermic by about 28 kcal and just as unlikely under the observed conditions. Hence only the ion-pair pathway is left.

For the process $CH_3\overline{CHOO}$ plus methanol we estimate by our usual methods (Tables I and II)

$$CH_3\overline{CHOO} + CH_3OH \rightleftharpoons [CH_3CHO_2H^+\cdots\bar{O}CH_3] \quad \text{(XLI)}$$

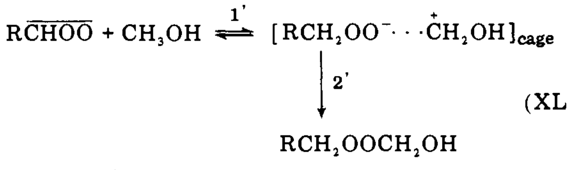
$$\Delta H°_{ip(r)}[CH_3OH(l)] \simeq 0 \text{ kcal/mol}$$

We have assumed that $IP(CH_3\dot{C}HO_2H) = IP(CH_3\dot{C}HOH) = 6.85$ eV (Table II) and employed $D = 34$ for CH_3OH at $T < 273$ K. Even with the relatively large uncertainties in the overall calculation, including the stabilization energy of the carbonyl oxide, this result predicts an extraordinarily effective scavenging of carbonyl oxides by alcohols in agreement with observations.



(XLII)

It is of interest to note that the carbonyl oxides are isoelectronic in oxide structure with the O_3 molecule and hence it is not surprising that they have parallel heterolytic pathways. For the hydride ion transfer



$$\begin{tikzcd} R\overline{CHOO} + CH_3OH \arrow[r, shift left, "1'"] & {[RCH_2OO^-\cdots\overset{+}{C}H_2OH]_{cage}} \arrow[l, shift left] \arrow[d, "2'"] \\ & RCH_2OOCH_2OH \end{tikzcd}$$

(XLIII)

we estimate $\Delta H°_{ip(r)}[CH_3OH(l)] \sim 1$ kcal/mol, so it is a thermodynamically slightly less favored path. It is also kinetically less favored since the proton exchange is enhanced by a strong electrostatic, H-bond interaction between the terminal carbonyl oxide O atom and the alcoholic OH bond.

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Gas-Phase Acid-Induced Nucleophilic Displacement Reactions. Stereochemistry of Inter- and Intramolecular Substitutions at Saturated Carbon[1]

Maurizio Speranza* and Giancarlo Angelini

Contribution from the Laboratorio di Chimica Nucleare del C.N.R.,
Area della Ricerca di Roma, C.P. 10-00016 Monterotondo Stazione, Rome, Italy.
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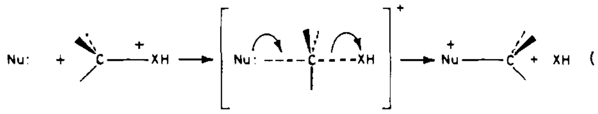
Abstract: The stereochemistry of gas-phase nucleophilic displacement by water on a number of positively charged intermediates was investigated under different experimental conditions. The ionic intermediates were generated in the gas phase at atmospheric pressure by attack of radiolytically formed Brønsted (CH_5^+, $C_2H_5^+$) and Lewis ($C_2H_5^+$, $CH_3FCH_3^+$) acids on selected mono- and bifunctional substrates. Isolation and identification of their neutral substituted products allowed us to demonstrate that, under the used experimental conditions, gas-phase acid-induced inter- and intramolecular nucleophilic displacement reactions occur via predominant (64–98%) *inversion* of configuration at the reaction center. The yield and the stereoisomeric distribution of the substituted products were found to depend on either the nature of the gaseous acid used to generate the charged intermediates or the concentration of the added base (NH_3 or H_2O). Product distribution from bifunctional substrates is characterized by the presence of minor amounts of substituted derivatives retaining the original configuration of their neutral precursors. Their formation is ascribed to the occurrence of an extensive neighboring group participation effect (an HO-3 process) on the displacement reaction, resulting in a double *inversion* of the reaction centers. A mechanistic model is proposed for gas-phase nucleophilic substitutions at atmospheric pressures, and compared with those from related low-pressure ICR (ion cyclotron resonance mass spectrometry) and solution-chemistry studies.

Introduction

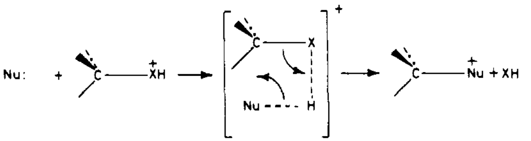
One of the most serious limitations of the mechanistic studies of gas-phase ion-molecule reactions is the almost complete lack of information on the stereochemistry of the processes investigated and the identities of their neutral products. The sporadic application of different experimental techniques, whose common features are the isolation of the neutral products and the determination of their structure, only scratched the surface of this problem. An interesting contribution was provided by a sophisticated trapped-ion ICR experiment carried out by Lieder and Brauman,[2] who elucidated the stereochemistry of a single negative-ion displacement reaction via the detection of the neutral products. However, this powerful technique, as well as other mass-spectrometric approaches, has left many other stereochemical questions unanswered, as demonstrated by the limited number of ion-molecule reaction mechanisms investigated and by the rarity of unambiguous data concerning their stereochemistry. A typical case is represented by the proton-induced nucleophilic displacement reactions at saturated carbon, a process frequently observed in mass spectrometry[3] (Nu: = nucleophile, X = n-donor center, R = alkyl group). As to the mechanism, it is still uncertain whether process (1) involves direct intermolecular substitution (2a),[4]

$$\text{Nu:} + \text{RXH}^+ \longrightarrow \text{NuR}^+ + \text{XH} \qquad (1)$$

i.e., a process corresponding exactly to the S_N2 type of solution chemistry (Walden inversion), or instead the more complex pathway (2b), leading to the retained substituted product via



(I)
(2a)



(II)
(2b)

the formation of the proton-bound complex (II).[5-7]

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