filtrate with preparative TLC (silica gel, hexane),[18] followed by crystallization from hexane. For **10**: mp 211 °C; IR 1880, 1430, 1270, 1255, 1100, 880, 840 cm^{-1}; mass spectrum *m/e* 704 (M^+); ^1H NMR δ -0.13 (18 H, s, Me_3Si), 0.28 (18 H, s, Me_3Si), 7.2-8.0 (20 H, m, ring protons); ^{13}C NMR δ 2.08 (q, CH_3Si), 6.49 (q, CH_3Si), 12.60 (s, $C(SiMe_3)_2$), 59.28 (s, $=C(SiMe_3)_2$), 60.71 (s, $=C(SiPh_2)_2$), 127.33 (d, Ph), 129.40 (d, Ph), 136.10 (d, Ph), 138.69 (s, Ph), 196.93 (s, =C=). Anal. Calcd for $C_{40}H_{56}Si_6$: C, 68.11; H, 8.00. Found: C, 68.10; H, 7.79. For **11**: mp 203 °C; IR 1885, 1430, 1265, 1255, 1105, 840 cm^{-1}; mass spectrum *m/e* 704 (M^+); ^1H NMR δ -0.21 (6 H, s, MeSi), 0.19 (6 H, s, MeSi), 0.23 (18 H, s, Me_3Si), 0.73 (6 H, s, MeSi), 7.0-7.9 (20 H, m, ring protons); ^{13}C NMR δ 1.75 (q, CH_3Si), 3.57 (q, CH_3Si), 5.06 (q, CH_3Si), 7.08 (q, CH_3Si), 10.26 (s, $C(SiMe_2Ph)_2$), 61.03 (s, $=C(SiMe_3)_2$), 61.42 (s, $=CSiPh_2$), 127.07 (d, Ph), 127.59 (d, Ph), 128.56 (d, Ph), 129.60 (d, Ph), 135.38 (d, Ph), 136.10 (d, Ph), 138.49 (s, Ph), 142.07 (s, Ph), 195.05 (s, =C=). Anal. Calcd for $C_{40}H_{56}Si_6$: C, 68.11; H, 8.00. Found: C, 67.86; H, 8.03.

Thermolysis of 8 in the Presence of Anthracene. A mixture of 50 mg (0.071 mmol) of **8** and 90 mg (0.505 mmol) of anthracene was heated at 250 °C for 3 h in a sealed glass tube. The reaction mixture was chromatographed by TLC (silica gel, hexane) to give 13 mg (34% yield) of anthracene adduct **12** and 20 mg (40% yield) of **10**. For **12**: mp 173 °C; IR 1900, 1425, 1245 cm^{-1}; ^1H NMR δ -0.13 (18 H, s, Me_3Si), 4.32 (1 H, s, HCSi), 4.79 (1 H, s, HCC(Si)=), 7.8-8.5 (18 H, m, ring protons); exact mass 542.2303 (calcd 542.2281).

Thermolysis of 8 in the Presence of a Tenfold Excess of Methanol. A mixture of 81 mg (0.115 mmol) of **8** and 50 μL (39 mg, 1.22 mmol) of dry methanol was heated in a 1.3-mL sealed glass tube at 250 °C for 30 min. The yields of the products **10**, **13**, **14**, **15**, **16**, and **17** were determined to be 27, 25, 6, 16, 14, and 7% by ^1H NMR spectroscopic analysis. Compounds **13**, **14**, and **15** were separated by preparative VPC. For **13**: IR 1435, 1270, 1260, 1115 cm^{-1}; ^1H NMR δ -0.02 (18 H, s, Me_3Si), 0.05 (1 H, s, HC), 3.45 (3 H, s, CH_3O), 7.25-7.75 (10 H, m, ring protons); exact mass ($M^+ - CH_3$) 357.1548 (calcd 357.1526). For **14**: IR 1905, 1435, 1255, 1120, 1090 cm^{-1}; ^1H NMR δ 0.16 (18 H, s, Me_3Si), 3.55 (3 H, s, CH_3O), 4.30 (1 H, s, HC=C), 7.2-7.8 (10 H, m, ring protons); exact mass 396.1776 (calcd 396.1761). For **15**: IR 2160, 2110, 1435, 1120, 1090 cm^{-1}; ^1H NMR δ 0.00 (18 H, s, Me_3Si), 1.25 (1 H, s, $HC(SiMe_3)_2$), 3.55 (3 H, s, CH_3O), 7.2-7.8 (10 H, m, ring protons); exact mass 396.1780 (calcd 396.1761). Compound **10** was isolated by TLC (silica gel, hexane). All spectral data for **10**, **16**, and **17** were identical with those of authentic samples.

Thermolysis of 8 in a Large Excess of Methanol. A mixture of 50 mg (0.071 mmol) of **8** and 100 μL of dry methanol in a sealed glass tube was heated at 210 °C for 1 h. The reaction mixture was crystallized from methanol[19] to give 35 mg (67% yield) of a mixture of **16** and **17**: IR 1890, 1875, 1425, 1265, 1250, 1100, 1070 cm^{-1}; ^1H NMR δ 0.01 (18 H, s, Me_3Si), 0.03 (18 H, s, Me_3Si), 0.10 (18 H, s, Me_3Si), 0.12 (18 H, s, Me_3Si), 0.85 (1 H, s, $HC(SiMe_3)_2$), 3.56 (3 H, s, CH_3O), 3.62 (3 H, s, CH_3O), 4.83 (1 H, s, HC=C), 7.1-8.0 (40 H, m, ring protons); exact mass 736.3281 (calcd 736.3260).

Isomerization of 7. Compound **7** (20 mg, 0.028 mmol) in a sealed glass tube was heated at 255 °C for 20 min. The ^1H NMR spectrum of the reaction mixture showed quantitative formation of **9**. The mixture was chromatographed by preparative TLC (silica gel, mixed solvent of benzene and hexane (1:5)) to give 13 mg (65% yield) of **9**. All spectra data were identical with those of the authentic sample.

Reaction of 8 with Elemental Sulfur. A mixture of 60 mg (0.085 mmol) of **8** and 60 mg (0.234 mmol) of elemental sulfur in a sealed glass tube was heated at 250 °C for 30 min. Product **18** was isolated by preparative TLC (silica gel, hexane) and crystallized from hexane to give 44 mg (70% yield) of pure **18**: mp 235 °C; IR 1820, 1420, 1245, 1095, 835 cm^{-1}; mass spectrum *m/e* 736 (M^+); ^1H NMR δ -0.02 (18 H, s, Me_3Si), 0.03 (18 H, s, Me_3Si), 7.1-8.1 (20 H, m, ring protons). Anal. Calcd for $C_{40}H_{56}SSi_6$: C, 65.14; H, 7.65. Found: C, 64.92; H, 7.67.

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(18) Treatment of a mixture of **10** and **11** with preparative TLC afforded only **10**; compound **11** decomposed to give a nonvolatile product on silica gel.

(19) A ratio of **16** to **17** determined by the ^1H NMR technique did not change after crystallization.

Quenching of Aromatic Ketone Phosphorescence by Simple Alkenes: An Arrhenius Study

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Abstract: The phosphorescence of 4-carboxymethylbenzophenone in carbon tetrachloride solution is quenched by various alkenes. The kinetics follow Stern-Volmer kinetics. An Arrhenius plot of k_{ir}, the apparent second-order rate constant, yields activation energies of 1.77 kcal/mol for 1-pentene, 0.5 ± 0.1 kcal/mol for *cis*- and *trans*-2-pentene and 2-methyl-1-butene, and 0.2 kcal/mol for 2-methyl-2-butene. 2,3-Dimethyl-2-butene has a curved Arrhenius plot which indicates a change in the rate-determining step for the quenching process. This is interpreted to mean that triplet exciplex formation is partially diffusion controlled in the low-temperature domain and reversible at higher temperatures.

Introduction

Triplet exciplexes are elusive species. Often invoked, they are rarely observed.[1] Consequently their presence in particular photochemical reactions is often inferred on the basis of indirect evidence. The reaction of ketone triplet states with simple alkenes[2] is a classic case in which exciplexes were invoked to help rationalize results which deviated from expections based on studies of reactions of electrophilic radicals with alkenes.[3] Similar inferences have been drawn in the reports of ketone fluorescence quenching by

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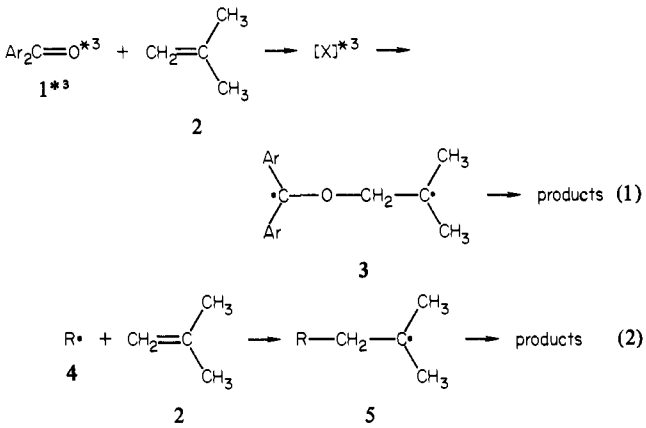
electron donors.[4] While it is generally accepted that some sort of electronically excited donor–acceptor complex is involved in these reactions,[2,4] there is no proof of its existence, and the question of whether the complex is formed reversibly or irreversibly is a matter of controversy. It has become an important matter to identify this species and to try to describe some of its properties.

Both Wagner[5] and Caldwell[6] have discussed thoroughly the evidence which led them and others to infer the presence of this exciplex. To summarize these arguments, triplet-state photoadditions to alkenes,[7] and "sensitized" cis–trans isomerization, involve formation of a biradical **3** as an intermediate.[8] While the factors affecting the formation of this biradical ought to be similar to those involved in radical addition to alkenes to give the analogous intermediate **5**, the differences in these reactions are in many ways more striking than the similarities (see eq 1 and 2).



Radical additions are very sensitive to steric effects with 1,2-disubstitution markedly reducing alkene reactivity.[9] Electrophilic radicals like $CF_3\cdot$ are also sensitive to the ionization potential of the alkene in their rates of addition, but the magnitudes of the steric effects are always comparable to or greater than the electronic effects.[9a]

Rates of ketone photoadditions are enhanced by increasing methyl substitution on alkenes; thus electronic effects here predominate over steric effects. Photoadditions to unsymmetric alkenes are less selective than radical additions to these alkenes.[2a] The "expected" inverse secondary deuterium isotope effect for rate-determining biradical formation is not found in the sensitized isomerization of *cis*- and *trans*-2-butene.[6] Rate constants for quenching of ketone triplets by alkenes are often much faster than one would anticipate for rate-determining biradical formation.[5]

In order to rationalize these observations, an additional intermediate[3] was introduced into the mechanism of the photoreaction. This species $[X]^{*3}$, which precedes biradical formation, was considered to have the properties of a donor–acceptor complex and to be in an electronically excited state. While it has never been observed, its putative presence serves to explain the linear dependence of the rate constant for ketone triplet quenching (k_{ir}) upon the ionization potential of electron-rich alkenes. Caldwell's detailed secondary deuterium isotope effect studies of the reaction of benzophenone with various butenes led to the conclusion that exciplex formation was rate limiting (i.e., irreversible).[6] In addition, Gupta and Hammond[10] have reported that, extrapolating to infinite alkene concentration, there is still an electronically excited intermediate quenchable by piperylene in the reaction of acetophenone and *cis*-2,2-dimethyl-3-hexene.

These results and their attendant conclusions still suffer important internal inconsistencies. It is still unclear why plots of log k_{ir} vs. IP (alkene) for different ketones give different slopes.[2c,11] It is most unusual for exciplexes to be formed irreversibly at rates slower by a factor of 1000 than diffusion controlled. In typical singlet-state exciplexes, from which emission can be observed, values of k_{ir} much less than k_{diff} are associated with reversible exciplex formation followed by rate-limiting decay or reaction of the exciplex.[12] It is also not clear how steric effects operate in biradical formation. If they enter into k_{ir}, they may be masking an even greater sensitivity to electronic factors than appears in log k_{ir} vs. IP plots.

In order to answer some of the questions posed by these dilemmas, we undertook a detailed Arrhenius study of the phosphorescence quenching in solution of an aromatic ketone by a series of simple alkenes. The ketone, 4-carboxymethylbenzophenone (B), whose spectroscopy we have thoroughly investigated,[13] is a typical substituted benzophenone. While our need to compare numerically these results with corresponding intramolecular reactions[14] dictated the use of this ketone, our results and conclusions should pertain to all lowest $^3(n\pi^*)$ ketones.

Experimental Section

The chromophore 4-carboxymethylbenzophenone was synthesized by the following method. 4-Benzoylbenzoic acid (purchased from Aldrich), 2.15 g, was esterified by refluxing it in 300 mL of methanol in the presence of trace sulfuric acid for 3 h. The reaction mixture was then made just basic with aqueous sodium hydroxide. A white solid precipitated out. Methanol was removed on the rotary evaporator, and the remaining solid was dissolved in benzene; the solution was washed twice with saturated aqueous sodium bicarbonate and three times with water. The benzene solution was dried with anhydrous sodium sulfate and benzene evaporated off. The 4-carboxymethylbenzophenone (B) obtained was recrystallized three times from carbon tetrachloride and sublimed once. The solvent carbon tetrachloride obtained from Burdick and Jackson (spectrograde, glass distilled) was further purified by a method already described.[15]

The quenchers tetramethylethylene and trimethylethylene were purchased from Aldrich; *cis*- and *trans*-2-pentene, 1-hexene, and 2-methyl-1-butene from Chemical Samples; 1,3-pentadiene from MCB; naphthalene from Fisher Scientific Co.; and *n*-hexane from BDH Chemicals. The quenchers were further purified just prior to use by the following methods (GC purities on $AgNO_3$ on Chrom P (HP) in a 10 ft × $^1/_8$ in. column at 30 °C are shown in parentheses): flash distillation over $LiAlH_4$ was used for tetramethylethylene (99.9%), trimethylethylene (100.0%), *cis*-2-pentene (95.5% cis and 4.5% trans), *trans*-2-pentene (96.2% trans and 3.8% cis), and 2-methyl-1-butene (99.9%). A spinning band column was used for distillation of 1-hexene (99.9%). 1,3-Pentadiene was fractionally distilled using a 6-in. Vigreux column, and naphthalene was recrystallized from carbon tetrachloride. *n*-Hexane was purified by a method already described[15a] (100% with no alkene detected).

Solutions containing 1.5×10^{-3} M B with varying concentrations of quencher in carbon tetrachloride were prepared. The range of concentrations differed for each quencher but was chosen so that the highest concentration quenched about 90% of the phosphorescence of B. Samples were placed in cells constructed from 13-mm o.d. Pyrex tubing, degassed

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by standard freeze–pump–thaw techniques,[15a] and sealed under vacuum in Pyrex tubes. Lifetimes (τ) for each of six concentrations of quencher were measured by flash photolysis,[15] and the rate constants, k_{ir}, were obtained from typical Stern–Volmer plots (eq 3). Signal averaging (of

$$1/\tau = 1/\tau_0 + k_{ir}[\text{quencher}] \quad (3)$$

three to five traces) gave exponential decay traces which yielded lifetime values with a precision of ±3%, and Stern–Volmer plots with correlation coefficients better than 0.99. Rate constants k_{ir} were determined at many temperatures between −20 and 100 °C and treated in an Arrhenius fashion. The temperature control apparatus has already been described.[15a]

Some of the quenchers, particularly the lower boiling disubstituted alkenes (bp 31–37 °C), gave erratic results at higher temperatures. At temperatures even as low as 35 °C, poor Stern–Volmer plots were obtained. This resulted in unpredictable and irreproducible rate constants. Usually at very high temperatures (>80 °C) good Stern–Volmer plots would again be obtained, with the Arrhenius behavior following that at low temperatures (<30 °C). After much effort to reproduce and explain chemically this behavior, we realized that the effect came about physically.

At the beginning of this study, we used cells which, after sealing, had a significant vapor space (5 to 6 mL) above the liquid. By redesigning the cells to keep this vapor space to a minimum (<1 mL), and by ensuring that the sample tubes were entirely contained within the heated block, this unusual behavior disappeared. We reasoned that volatile quenchers either preferentially occupied the vapor space or selectively condensed on cool spots on the wall of the sample tube.

Two other artifacts made these experiments more difficult than we had anticipated. First, all batches of CCl_4, even after purification, contain traces of a volatile impurity (phosgene?). In our original sample tubes, the lifetime of B went through a minimum at 25 °C as the temperature was varied, and a maximum near 80 °C. This curious effect disappeared when we used either well-aged purified solvent or the sample tubes which minimized the vapor space above the sample. Since this effect was identical in all samples, the Stern–Volmer slopes (eq 3) were unaffected. Second, all samples containing benzophenone and a source of abstractable hydrogens give rise to a highly fluorescent impurity with a short fluorescent lifetime (<10 ns).[15b,c] While this emission was only a minor annoyance in measuring the decay times of the much longer lived phosphorescence of B, it did make it impossible to look for a short component to the emission of B when our inference of extensive exciplex formation would predict double exponential decays.

Results and Discussion

When exciplex emission cannot be observed, the presence of an exciplex is very difficult to establish. It has been argued that positive Arrhenius slopes associated with k_{ir} (which imply apparent negative activation energies) provide definitive evidence for exciplex formation; raising the temperature promotes dissociation of the transient complex to regenerate the light-emitting excited state.[16] According to this criterion, several triplet exciplex forming pairs have been found. Steel found that quenching of benzaldehyde phosphorescence by toluene gave an apparent $E_{a,ir}$ of −2.4 kcal/mol in acetonitrile.[17] More recently Kuzmin[18] reported an extensive series of experiments in which flash photolysis followed by triplet–triplet absorption measurements were used to follow the temperature dependence of quenching aromatic hydrocarbon triplets by nitrobenzenes in acetonitrile. Here 1,2-benzanthracene showed an apparent negative activation energy. The quenchings of triplet cyclic enones by cyclohexene[19] and of triplet acetone by norbornene,[20] have shown small positive activation energies (ca. 1 kcal/mol). These values are less than that associated with viscous flow and are consistent with an exciplex mechanism, although not definitive.

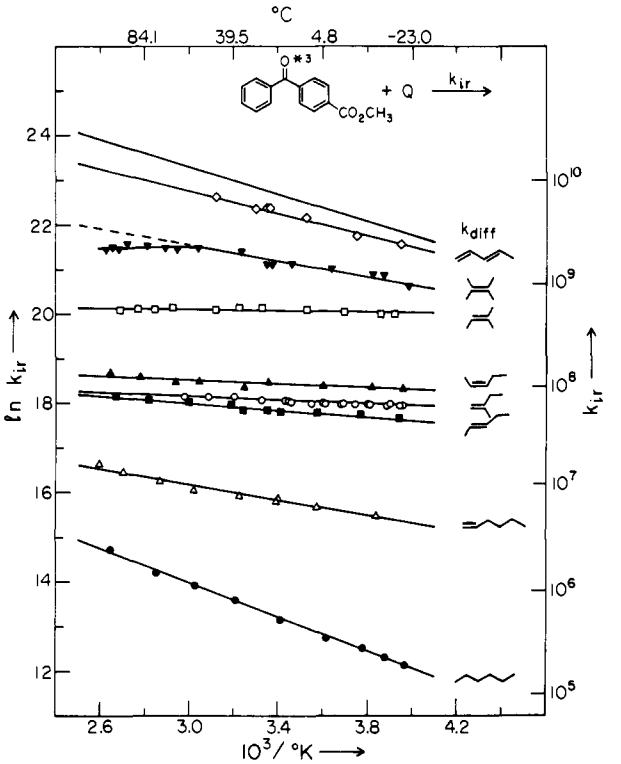

Figure 1. Arrhenius plots of the quenching of B*[3] by various quenchers.

Rate constants for the reactions we have studied were calculated from the phosphorescence lifetimes according to eq 3 and treated by the simple Arrhenius equation

$$k_{ir} = A_{ir} \exp(-E_{a,ir}/RT) \quad (4)$$

The corresponding Arrhenius plots are shown in Figure 1. Also included in Figure 1 are data for the reaction of B* with *n*-hexane, which quenches by a hydrogen-abstraction mechanism, the reaction of B* with 1,3-pentadiene, which quenches by triplet energy transfer at the diffusion-controlled rate, and a plot of the "theoretical" value of k_{diff}, the diffusion-controlled rate constant, calculated from the Debye equation

$$k_{diff} = 8\pi RT/3000\eta \quad (5)$$

using literature values[21] of the viscosity [η] of carbon tetrachloride at various temperatures.

One remarkable aspect of the data is that, for hexane and the mono- and disubstituted alkenes, the Arrhenius plots share a common intercept, even though at room temperature the reactivities of these compounds differ by a factor of 10^3. This behavior is a consequence of very different Arrhenius activation energies E_A which decrease from 3.8 kcal/mol for hexane to 1.8 kcal/mol for 1-hexene to ca. 0.5 kcal/mol for *cis*- and *trans*-2-pentene and for 2-methyl-1-butene; i.e., E_A decreases with increasing quencher reactivity. It appears that the four alkenes react by a similar mechanism. In each case E_A is significantly smaller than that for diffusion calculated from the temperature dependence of the solvent viscosity. These are the alkenes for which irreversible exciplex formation has been inferred on the basis of isotope effect studies.[6]

These data taken by themselves are not necessarily inconsistent with rate-determining exciplex formation. It is possible to have a reaction proceed with zero activation energy and still occur much slower than the diffusion limit if the entropy requirements are so strict that only a small fraction of the encounters between the

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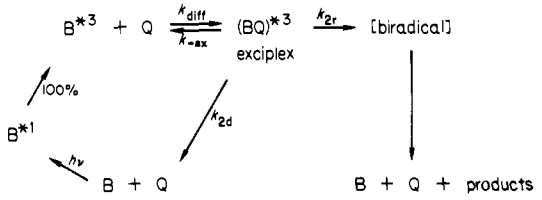
(21) When one of the exciplex partners is an aliphatic amine, geometry changes accompany exciplex formation, and the corresponding rate constant is smaller than k_{diff}. See, for example: (a) Nakashima, N.; Mataga, N.; Yamanaka, C. *Int. J. Chem. Kinet.* **1973**, *5*, 833–839. (b) Meeus, F.; Vander Auweraer, M.; Dederen, J. C.; De Schryver, F. C. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 220–223.

Scheme I



species is effective at finding the right geometry for reaction. A preexponential factor of 10^8 corresponds to $\Delta S^* = -22$ cal K^{-1} mol^{-1}, a typical value for a bimolecular reaction involving a modestly "tight" transition state, in which the translational and rotational entropy of the reactants is compensated to some degree by low-frequency vibrational entropy in the transition state. By assuming irreversible exciplex formation, one would have to conclude that the transition state for exciplex formation has a geometric requirement similar to that for hydrogen abstraction.

The more reactive alkenes show a different pattern of reactivity. The Arrhenius plot for trimethylethylene is nearly parallel to those of the disubstituted ethylenes. The corresponding plot for tetramethylethylene [TME) is curved.[22] When these data are fit to two straight lines intersecting at 40 °C one sees that the high-temperature slope is again nearly zero, whereas at low temperature there is an appreciable activation energy. For 1,3-pentadiene, which should quench B^{*3} by triplet energy transfer at the diffusion-controlled rate, one finds E_A very close to that predicted from the temperature dependence of the solvent viscosity, and an intercept typical of diffusion-controlled processes.

Tetramethylethylene plays a crucial role in the conclusions we wish to draw. At very high temperatures, where carbon tetrachloride is very fluid, its Arrhenius behavior is virtually flat, implying a near-zero apparent activation energy. At lower temperatures, as the solvent viscosity increases, there is a change in slope, with E_A approaching that of viscous flow. The limiting A factor of tetramethylethylene for the low-temperature data is also close to the value expected for a diffusion-controlled reaction. We infer that below 40 °C quenching by TME is partially diffusion controlled, and that, in this temperature domain, exciplex formation is rate limiting. The change in slope in the Arrhenius plot for TME at 40 °C means a change in the rate-limiting step. This requires that exciplex formation be reversible at high temperatures.

Kinetic Scheme. In order to interpret our results in more detail, it is necessary to analyze our data in terms of a kinetic scheme which serves as a postulated mechanism for the reaction (see Scheme I). Irradiation of B produces the excited singlet state which rapidly decays with unit efficiency to its triplet state. B^{*3} can decay by phosphorescence with a rate constant k_p or radiationlessly with a rate constant k_d. In competition with these processes, it can interact with an alkene quencher Q to form an exciplex which in turn decays radiationlessly to products (via an intermediate biradical when Q is an alkene) or to B and Q in their ground electronic states.

According Scheme I, B^{*3} and Q react to form an exciplex on every encounter. This phenomenon is well documented in the case of singlet exciplexes.[23-25] We use the term k_{diff} to describe this diffusion-controlled process and k_{-ex} to describe the rate constant for dissociation of the exciplex back to B* and Q. We use the rate constant $k_2 = (k_{2r} + k_{2d})$ to describe the sum of pathways for exciplex decay.

The "observed" rate constant from eq 3 is related to the rate constants in Scheme I according to eq 6. In employing this

$$k_{ir} = k_{diff}k_2/(k_{-ex} + k_2) \qquad (6)$$

scheme, one often draws attention to two limiting situations. The first is the diffusion controlled or low-temperature limit where $k_2 \gg k_{-ex}$ and $k_{ir}^{LTL} = k_{diff}$. The second is the preequilibrium or high-temperature limit where $k_2 \ll k_{-ex}$ and $k_{ir}^{HTL} = (k_{diff}/k_{-ex})k_2$. It is often not made clear when these limiting cases hold, since k_{ir} is often within one or two orders of magnitude of k_{diff}, implying that k_2 and k_{-ex} values are comparable. In the intermediate region, where $k_{ir} < k_{diff}$ but where diffusion still has an important effect on the magnitude of k_{ir}, the reaction may be considered to be partially diffusion controlled.

Table I. Activation Energies and A Factors for the Quenching of 4-Carboxymethylbenzophenone in CCl_4[a]

quencher	$k_{ir}^{20°}$, M^{-1} s^{-1}	A, s^{-1}	E_A, kcal/mol
n-hexane	5.1×10^5	3.74×10^8	3.82 ± 0.09[b]
1-hexene	7.1×10^6	1.55×10^8	1.77 ± 0.12
trans-2-pentene	5.4×10^7	2.05×10^8	0.75 ± 0.07
2-methyl-1-butene	7.2×10^7	1.57×10^8	0.50 ± 0.04
cis-2-pentene	1.0×10^8	2.1×10^8	0.42 ± 0.10
2-methyl-2-butene	5.5×10^8	7.4×10^8	0.19 ± 0.06
2,3-dimethyl-2-butene		2.6×10^9 [c,d]	0.15 ± 0.17[c]
2,3-dimethyl-2-butene	1.6×10^9	(3.3×10^{10})[d,e]	1.75 ± 0.12[e]
1,3-pentadiene	5.0×10^9	3.2×10^{11}	2.48 ± 0.13

[a] Corrected for solvent density changes with temperature. [b] One standard deviation. [c] Above 40 °C. [d] Extrapolated value in parentheses. [e] Below 40 °C.

The extent to which diffusion effects perturb the kinetics of activation-controlled reactions depends upon the precision at which data can be obtained. Since absolute rate constants for quenching reactions are rarely known with a precision of less than ±5%, one can say that a reaction is effectively in the preequilibrium limit for the mechanism given in Scheme I when $k_{ir} \leq 0.05k_{diff}$.

For our results, only trimethylethylene and TME have k_{ir} values that exceed $0.05k_{diff}$. As we will discuss later, proper interpretation of these results requires correction for diffusion effects. We first consider interpretation of the Arrhenius plots in the cases of limiting behavior.

The Arrhenius behavior of k_{ir} in the preequilibrium limit can be expressed as

$$\log k_{ir}^{HTL} = \log \left[\frac{A_{diff}A_2}{A_{-ex}}\right] - \frac{E_{a,2} + \Delta H_{ex}}{RT} \qquad (7)$$

where ΔH_{ex}, the binding enthalpy of the exciplex, is equal to $(E_{a,diff} - E_{a,-ex})$. In the diffusion-controlled limit, k_{ir} can be expressed as

$$\log k_{ir}^{LTL} = \log A_{diff} - E_{a,diff} \qquad (8)$$

Table I shows that the Arrhenius activation energies associated with quenching by mono-, di-, and trisubstituted alkenes are quite low: 1.8, 0.5, and 0.2 kcal/mol, respectively. These values are much less than $E_{a,diff}$ (=3.1 kcal/mol; see below) and are consistent with the binding energy in the exciplex ($\Delta H < 0$) almost exactly counterbalancing the activation energy for collapse of the exciplex to the biradical.

Correction of Diffusion Effects. A simple rearrangement of eq 6 leads to

$$\frac{k_{-ex}}{k_2} = \frac{k_{diff} - k_{ir}}{k_{ir}} \qquad (9)$$

This equation, first applied to ketone photochemistry by Evans,[25] permits one to correct for diffusion effects if values of k_{diff} are known. Values at various temperatures for k_{diff} can in principle be obtained by Stern–Volmer analysis of diffusion-controlled emission quenching at each temperature. Because of the scatter and the need to determine A_{diff} with some accuracy, we resorted to a more indirect approach.

Using literature viscosity values[21] and eq 5, we calculate a "theoretical" value of $E_{a,diff}$ for carbon tetrachloride to be 3.08

(22) Additional experiments of temperatures between 100 and 190 °C show an Arrhenius slope with $E_a = 0.4 \pm 0.3$ kcal/mol for quenching by tetramethylethylene.

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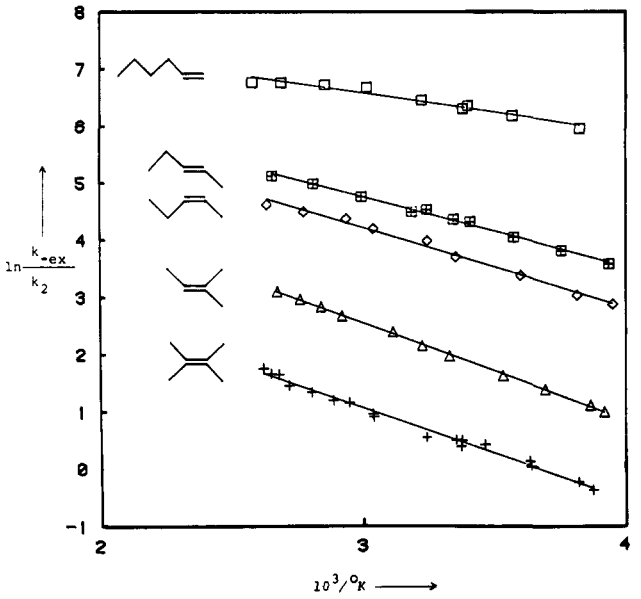

Figure 2. Arrhenius behavior of k_{ex}/k_2.

Table II. Activation Energy Differences and A Factor Ratios for Phosphorescence Quenching Reactions[a,b]

quencher	A_{-ex}/A_2	ΔE_a, kcal/mol	E_a^{cor}, kcal/mol
2,3-dimethyl-2-butene	400	3.25	−0.2
2-methyl-2-butene	2200	3.40	−0.3
cis-2-pentene	4600	2.79	+0.3
trans-2-pentene	4500	2.44	+0.6
1-hexene	5700	1.38	+1.7

[a] ΔE_a, the difference in activation energy for exciplex dissociation and exciplex deactivation, is obtained from eq 9 and 10. [b] E_a^{cor} is obtained from eq 11.

kcal/mol. This assumes that eq 5 gives a better description of the sensitivity of k_{diff} to temperature than absolute values of k_{diff}. Our data for k_{ir} with 1,3-pentadiene and for naphthalene were then fit to eq 4, assuming $E_{a,diff}$ = 3.08 kcal/mol, yielding A_{diff} = 8.95×10^{11} s^{-1} as an optimum value.

The ratio (k_{-ex}/k_2), obtained from eq 9, is plotted in Arrhenius fashion in Figure 2. All plots are linear. This is expected for 1-hexene and the 2-pentenes since their quenching rate constants are much smaller than diffusion controlled. What is remarkable is that the data for TME, which gave curved Arrhenius plots for k_{ir}, become linear when plotted according to eq 9. This fact emphasizes that diffusion effects are responsible for the original curvature and corroborates the conclusion that exciplex formation is rapidly reversible above 40 °C.

The slopes of the plots in Figure 2 yield the activation energy difference

$$\Delta E_a = E_{a,-ex} - E_{a,2} \quad (10)$$

These values are listed in Table II. They show that the activation barrier for exciplex dissociation is always much higher than that for exciplex deactivation. The diffusion-corrected activation energy for the overall reaction can be determined from

$$E_a^{cor} = E_{a,diff} - \Delta E_a \quad (11)$$

Values of E_a^{cor} correspond very closely to values of $E_{a,ir}$ obtained from Figure 1 in the case of alkenes which react much slower with B*³ than the diffusion-controlled limit. When k_{ir} is compared with k_{diff} at any of the temperatures examined, eq 11 gives a more reliable value for the energy barrier for the activation-controlled process than does eq 4.

Table II also lists values of A_{-ex}/A_2 calculated from our data. These values vary from 400 for TME to 5700 for 1-hexene. Although individual values of A_{-ex} and A_2 cannot be determined,

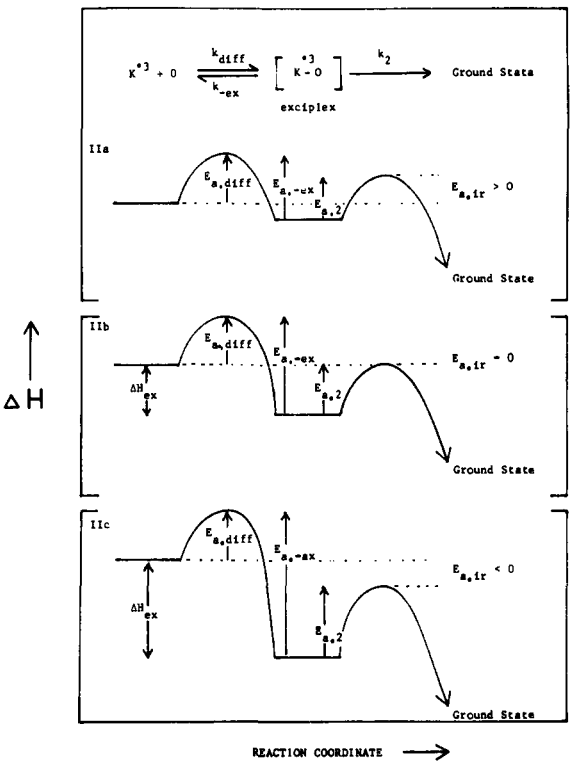

Figure 3. Enthalpy-reaction coordinate profile for a positive activation energy (IIa), an activation energy of zero (IIb), and a negative activation energy (IIc).

we can attempt to rationalize these results by looking at two limiting situations.

(i) If A_{-ex} is constant throughout the series of alkenes, then A_2 increases with quencher reactivity. This requires that the k_2 transition state resemble the exciplex more closely for the more reactive alkenes, implying that the more charge-transfer character in the exciplex, the more its geometry resembles that for the transition state for exciplex deactivation or biradical formation.

(ii) If A_2 is constant throughout the series of alkenes, then A_{-ex} decreases for the more reactive quenchers. This result is consistent with the idea that the greater the charge-transfer character in the exciplex, the more extensive the geometric and solvent reorganization necessary for exciplex dissociation. Both points of view have merit, but it is worth noting that the magnitude of the overall differences is small.

Another way of looking at our results is in terms of a reaction coordinate diagram (Figure 3) in which enthalpy ΔH is plotted on the ordinate and the Arrhenius activation energy is treated as an enthalpy. In this plot the second step is pictured as the rate-limiting reaction. Its activation energy is *less* than that of the diffusion step because *entropic* factors intervene to make this the slowest step. A negative activation energy (e.g., TME) can be pictured as deriving from a sequence of reactions whose slowest step (because of entropy and, hence, free energy) lies lower in enthalpy than the starting reagents B*³ and Q.

Asymptotic Behavior in the High- and Low-Temperature Limits. An interesting consequence of eq 9 is that the asymptotes of the Arrhenius plots can be determined. All quenchers approach the diffusion limit in the extremes of low temperature (neglecting differences in translational diffusion constants and solvent freezing point). The high-temperature limit is that in which k_{ir} is no longer influenced by diffusion. This value, k_{ir}^{HTL}, is obtained from k_{ir}^{HTL} = $(k_{diff}/k_{-ex})k_2$. Figure 4 shows the Arrhenius behavior of k_{ir}, k_{diff}, and k_{ir}^{HTL} for both trimethylethylene and tetramethylethylene. Note that one consequence of Scheme I is satisfied: that at the point where the ln k_{diff} line intersects the ln k_{ir}^{HTL}, the value should be greater than ln k_{ir} by ln 2 (i.e., $k_{ir} = k_{diff}/2$).

Additional Comments. First, we can speculate on the role of steric effects in the photoaddition of ketones to alkenes. The

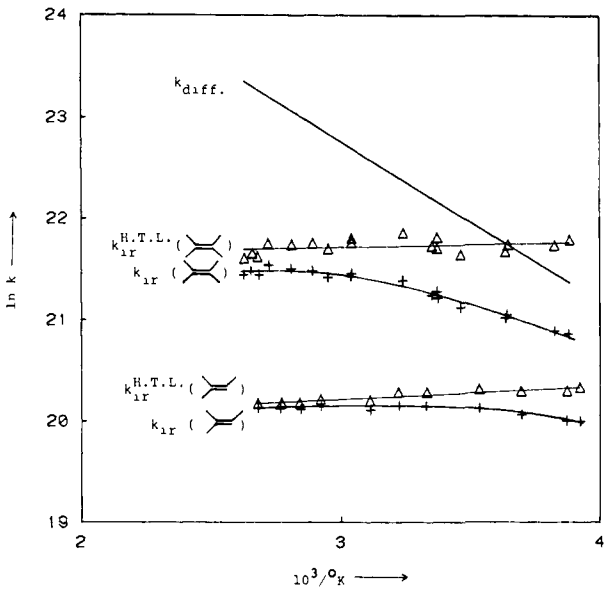

Figure 4. The Arrhenius behavior of k_{ir} and k_{ir}^{HTL}, for tetramethylethylene and trimethylethylene, and k_{diff}.

substituted olefins, having lower IP's, have more negative values of $\Delta H°_{ex}$. These molecules also have correspondingly larger values of $E_{a,2}$. Consequently steric effects play an important role in decreasing the rate of biradical formation and make the apparent sensitivity of k_{ir} to quencher ionization potential less than that one might observe if one could measure $\Delta H°_{ex}$ and the equilibrium constant for exciplex formation.

Second, virtually all *gas-phase* additions of multiatom radicals to alkenes show A factors of ca. 1×10^8 s^{-1}. If exciplex decay to biradical is rate determining, its A factor should be similar; the entropy of biradical formation from the separated reactants is independent of whether an exciplex intermediate precedes the reaction transition state. Third, correlations of log k_{ir} vs. IP must be interpreted with care. Our data indicate that the slopes of such plots are temperature dependent and that steric effects operate to oppose the dependence of $\Delta H°_{ex}$ upon quencher ionization potential.

Summary

An Arrhenius study has been carried out for quenching of phosphorescence in carbon tetrachloride of a substituted benzophenone, 4-carboxymethylbenzophenone, by a series of simple alkenes. The Arrhenius plots are characterized by very low activation energies (0 to 1.8 kcal/mol), and, for the less reactive alkenes, A factors typical for the addition of radicals to carbon–carbon double bonds.

A new criterion has been established for identifying a nonemissive exciplex, namely a curved Arrhenius plot in an emission quenching reaction, signifying a change in the rate-limiting step with a change in temperature. This change was associated with a transition from diffusion-controlled exciplex formation at low temperatures to reversible exciplex formation followed by rate-determining exciplex deactivation at high temperatures.

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Unimolecular Reactions of Ionized Alkanes

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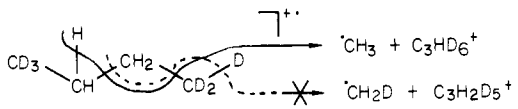
Abstract: The unimolecular reactions of several $C_nH_{2n+2}^{+\cdot}$ radical cations are discussed in terms of species involving an incipient carbonium ion coordinated to a radical. These species can be formed by stretching the appropriate bond in the ionized alkane. Subsequent isomerization of the incipient carbonium ion can give rise to rearranged structures in which a 1,2-alkyl shift has effectively occurred. By means of such mechanisms, much of the previously reported data concerning decomposition of ionized *n*-butane can be explained; in particular, the results of ^{2}H-labeling studies can be interpreted. In addition, new labeling data are reported for ionized *n*-pentane and isopentane; the results indicate that both 1,2-methyl and 1,2-ethyl shifts precede or accompany dissociation of these $C_5H_{12}^{+\cdot}$ species. Previously published ^{13}C- and ^{2}H-labeling data on ionized *n*-heptane are also considered; these results can be understood in terms of competing 1,2-methyl, -ethyl, and -propyl shifts.

Introduction

The unimolecular reactions of ionized alkanes have been the subject of extensive research.[2-17] Although the chemistry of alkanes is generally regarded as being simple, because of the absence of functional groups, this is certainly not true for the ionized compounds. Extremely complex behavior is frequently observed, even for relatively small $C_nH_{2n+2}^{+\cdot}$ species; loss of alkyl

Scheme I



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