

Reactions of Triplet Decafluorobenzophenone with Alkenes. A Laser Flash Photolysis Study

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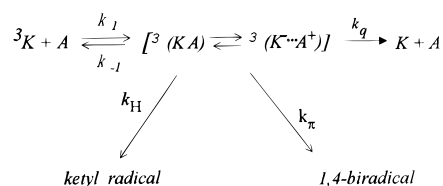
Received: January 2, 1997[⊗]

Rate constants for the reactions of triplet decafluorobenzophenone (³DFB) with 30 alkenes have been measured, with values in the range 10⁷–10⁹ L mol⁻¹ s⁻¹. The rate constant increases upon substituting electron-donating groups on the double bond, whereas it decreases upon substituting electron-withdrawing groups. For cyclohexene and 2-butene, the rate constant increases with increasing methyl substitution at the double bond, suggesting that steric effects play a minor role in the reaction. Further, there is a linear correlation between log *k_r* (*k_r* = the second-order rate constant of the reaction of ³DFB and alkene) and the ionization potential of the alkene. The extent of hydrogen abstraction was determined by measuring the yield of the ketyl radical. Quantum yields for ketyl radical formation, Φ_K, increase with the ionization potential and the number of activated hydrogens, nH, on the alkene. The absolute values of Φ_K and a linear correlation between Φ_K/nH and ionization potential suggest that hydrogen abstraction is preceded by complex formation.

Introduction

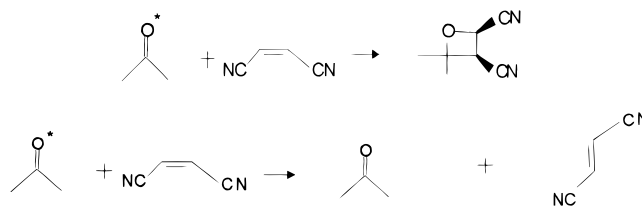
The photoreactions of excited ketones with alkenes have been the subject of numerous investigations because of the complexity of the mechanism and the synthetic utility of the reaction.^{1–32} The photocycloaddition of an olefin to a ketone, the Paternò–Büchi reaction, offers a simple route to the synthesis of oxetanes. The formation of the oxetane product may be accompanied by the concomitant formation of hydrogen-atom abstraction products and *cis*–*trans* isomerization of the alkene. The mechanism of the reaction has been the subject of intense experimental investigation.^{3–32} Two different mechanisms have been suggested.^{33,34} In one mechanism, called the “parallel approach”, the excited carbonyl behaves as a nucleophile, attacking the alkene in the plane of the double bond. In the other, called the “perpendicular approach”, the excited carbonyl behaves as an electrophile and attacks perpendicular to the plane of the double bond. Reactions of electron-rich alkenes are expected to favor the perpendicular approach, while reactions of electron-deficient alkenes are expected to favor the parallel approach. In both cases, the interaction leads to biradical formation.

The production of the biradical may be preceded by the formation of an intermediate charge-transfer complex or exciplex.^{9–32} The degree of charge-transfer stabilization of the complex depends on the relative reduction potentials of the ketone and the alkene.^{14,28}



The collapse of the complex can simply lead to the ground state reactants (*k_q*), or there can be an internal hydrogen abstraction

leading to the formation of a ketyl radical from the excited ketone and a carbon-centered radical from the alkene, or the complex can lead to a 1,4-biradical addition product. This latter biradical can either close to yield oxetane, decompose to regenerate the ketone with *cis*–*trans* isomerization of the alkene, or do both.^{29–32} For example, excited acetone reacts with the electron deficient molecule *cis*-1,2-dicyanoethene to give both the *cis*-oxetane and *trans*-1,2-dicyanoethene.



Triplet ketones abstract hydrogen from alkanes, alcohols, etc.^{35–37} They may also abstract from alkenes with allylic hydrogens. Hydrogen abstraction from alkenes may be either direct or may be preceded by the formation of the exciplex. A study of the reactions of several excited ketones with toluene and *p*-xylene has shown that both direct hydrogen abstraction and complex formation followed by hydrogen/proton transfer contribute to a different degree, depending on the reduction potential and triplet energy of the ketone.¹⁴

A few reports have appeared on the photochemistry of decafluorobenzophenone (DFB).^{38–43} Triplet DFB (³DFB) abstracts hydrogen from alkanes, alcohols, etc; it reacts with alkenes and aromatics; and it undergoes electron-transfer reactions with amines. In many of its reactions it exhibits a much higher reactivity than benzophenone.^{42,43} The yields of oxetanes from the photoreactions of perfluorinated carbonyl compounds with alkenes have been found to be higher than for nonfluorinated carbonyls.⁴⁴ The present paper presents an extensive study on the kinetics of the ³DFB reaction with alkenes. The parameters investigated include steric effects, the

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1997.

effect of substituting electron-donating or electron-withdrawing groups on the double bond, the position of the double bond, cyclic versus acyclic alkenes, the ionization potential of the alkene, and the effect of solvent. In order to understand the mechanism of hydrogen abstraction, we determined the quantum yield of ketyl radical formation and, from this, the rate constant for hydrogen abstraction, k_H .

Experimental Section

The spectrophotometric laser flash photolysis system was as described earlier.⁴⁵ Decafluorobenzophenone and decafluorobenzhydrol from Aldrich were used as received. Acetonitrile and carbon tetrachloride were spectroscopic grade. Ethyl vinyl ether, *trans*-1,2-dichloroethylene, 1-methyl-1-cyclohexene, 3-methyl-2-buten-1-ol, 2-methoxypropene, bicyclo[2.2.1]hepta-2,5-diene, trichloroethylene, crotonaldehyde, crotonic acid, 2-bromo-2-butene, furan, 3-chloro-1-butene, and tetrahydrofuran were from Aldrich. 2-Methyl-2-butene, 2,3-dimethyl-2-butene, 1,2-dimethylcyclohexene, 2-methyl-3-ethyl-2-pentene, *trans*-4-methyl-2-pentene, 3,3-dimethyl-1-butene, and *cis*-3-hexene were from Chemical Samples Co. 1-Hexene, *trans*-2-hexene, 1-methylcyclopentene, 2,4,4-trimethyl-1-pentene were from Baker. These alkenes were purified by passing through neutral alumina whenever necessary.

Solutions of DFB and the alkene in either carbon tetrachloride or acetonitrile were purged with high purity N₂ and continuously flowed through a 2 × 1 × 0.2-cm quartz cell where the excitation laser pulse intersects the probe beam from a Xe-arc lamp. The excitation laser pulse was at 351 nm (XeF). The absorbance of the DFB solution at 351 nm was maintained at about 0.3.

(The identification of commercial equipment or materials does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.)

Results and Discussion

The laser flash photolysis of decafluorobenzophenone yields the first excited singlet state, ¹DFB, which undergoes efficient intersystem crossing to the triplet, ³DFB.⁴⁶ The lifetime of the singlet is not known, but it would be expected to be similar to singlet benzophenone, which is 9.6 ps in acetonitrile.⁴⁷ This short lifetime precludes the singlet state from playing any role in the subsequent chemistry under the conditions of these experiments.

The reaction of ³DFB with alkenes can lead to physical quenching of the excited benzophenone, the formation and subsequent reactions of a 1,4-biradical, or, by hydrogen abstraction, the formation of a ketyl radical. The 1,4-biradicals formed in these reactions have very short lifetimes, <7 ns, and cannot be observed in our system.⁴⁸ The ketyl radicals, however, are long lived and monitored easily at 530 nm. In this study, we were interested in both the rate constants for the removal of ³DFB by the alkenes and in the extent that the reaction led to hydrogen abstraction. The overall rate constant for the reaction was determined by monitoring the decay of ³DFB at 560 nm. At this wavelength, the interference from ketyl radical absorption is negligible. The quantum yield of ketyl radical formation, Φ_K , was determined by using tetrahydrofuran as the reference reaction. ³DFB reacts with tetrahydrofuran with a rate constant of $2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. We assume this reaction is entirely due to hydrogen abstraction, yielding the ketyl radical with $\Phi_K = 1$.

We did not detect spectroscopically any transient which can be attributed to exciplex formation. The only transient that could be detected in this experiment after the quenching of the triplet was the ketyl radical. Due to the overlapping spectra of the triplet and the ketyl radical of DFB⁴³ over the entire absorption spectrum of the latter, it was not possible to determine whether the decay of the triplet leads to concomitant formation of the ketyl radical.

The second-order rate constant, k_r , for the overall reaction of ³DFB with an alkene was obtained from the slope of the dependence of the first-order decay rate, k_{obs} , of triplet DFB on the alkene concentration as given in eq 1,

$$k_{\text{obs}} = k_0 + k_r[\text{alkene}] \quad (1)$$

where k_0 is the decay rate of ³DFB in the absence of added alkene. The second-order rate constants determined with acetonitrile and carbon tetrachloride as solvents are listed in Tables 1 and 2. Included in Table 1 are the ionization potentials of the alkenes.⁴⁹ The rate constant for reaction of ³DFB with alkenes varies from 2×10^7 to $6.5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. The least reactive alkenes are *trans*-1,2-dichloroethene, trichloroethene, crotonic acid (*trans*-2-butenic acid), and alkenes with a terminal double bond. The substitution of alkyl groups about the double bond increases the rate constant. For example, the rate constants for methyl-substituted cyclohexenes increases in the following order: cyclohexene < methylcyclohexene < 1,2-dimethylcyclohexene. Similarly the rate constant for acyclic alkenes increases as steric crowding increases, *cis*-3-hexene < *trans*-4-methyl-2-pentene < *trans*-2-hexene < 2-methyl-2-butene < 2,3-dimethyl-2-butene, but then levels off as the steric crowding increases further as indicated by 2-methyl-3-ethyl-2-pentene. The same trend is exhibited by alkenes with a terminal double bond.

On the other hand, substitution of electron-withdrawing groups on the double bond decreases the rate constant, as in the case of methacrylonitrile (2-methyl-2-propenenitrile), *trans*-1,2-dichloroethylene, and trichloroethylene. Even substitution at the β -carbon has a significant effect, e.g. 3-chloro-1-butene. Substitution of an electron-releasing group on the double bond, however, enhances the rate constant, as in the case of ethyl vinyl ether, 2-methoxypropene, and 2-bromo-2-butene.

In its reaction with alkenes, ³DFB exhibits a pattern of reactivity similar to that of ³BP (triplet benzophenone) except for the magnitude. The reactivity of ³DFB toward cycloalkenes is a factor of 10 or more greater than that of ³BP (the rate constants for ³DFB or ³BP with cycloalkene do not vary much with the ring size). For acyclic alkenes with terminal double bonds the reactivity ratio DFB/BP ~ 100 . As the number of substituents on the double bond increases, the difference in their reactivity narrows, however. For 2,3-dimethyl-2-butene the ratio is only 2.8.

Figure 1a shows a plot of $\log k_r$ versus the ionization potential of the alkenes for those reactions in which acetonitrile was the solvent. The points are scattered but follow a general trend with the rate constant increasing as the ionization potential (IP) decreases. The best fit of the points yields a slope of -1.1 eV^{-1} . The dependence of the rate constants on the IP of the alkene is consistent with the electrophilic mechanism involving a perpendicular approach. For carbon tetrachloride as the solvent, the plot $\log k_r$ versus IP is more scattered than that observed for acetonitrile (Figure 1b). Linear regression yields a slope -0.9 eV^{-1} . This small difference between nonpolar carbon tetrachloride and polar acetonitrile suggests a contribution from charge transfer during the reaction, probably due to exciplex formation.

TABLE 1: Rate Constants^a and Quantum Yields of Ketyl Radical Formation for Reactions of ³DFB with Alkenes in Acetonitrile, and the Ionization Potential of the Alkenes

alkene	IP, eV	Φ_K	$k_r \times 10^{-7}$, L mol ⁻¹ s ⁻¹	$k_H \times 10^{-7}$, L mol ⁻¹ s ⁻¹	$k_\pi \times 10^{-7}$, L mol ⁻¹ s ⁻¹
2-methyl-3-ethyl-2-pentene	8.17	0.48	389	190	200
2,3-dimethyl-2-butene	8.26	0.48	441	210	230
Bicyclo[2.2.1]hepta-2,5-diene	8.35	0.00	298	0	300
1,3-cyclohexadiene	8.4	0.09	582	52	530
1-methylcyclopentene	8.55	0.31	184	57	130
2-methoxypropene	8.64	0.0	207	0	210
1-methylcyclohexene	8.67	0.25	440	110	330
2-methyl-2-butene	8.68	0.12	139	17	120
ethyl vinyl ether	8.8	0.0	246	0	250
1,4-cyclohexadiene	8.82	0.64	187	120	67
furan	8.88	0.0	648	0	650
2,4,4-trimethyl-1-pentene	8.91	0.03	80	2.4	80
cyclohexene	8.95	0.11	194	21	170
cis-3-hexene	8.95	0.08	88.8	7.1	82
trans-2-hexene	8.97	0.11	46.5	5.1	41
trans-4-methyl-2-pentene	8.97	0.14	32.8	4.6	28
cyclopentene	9.01	0.18	119	21	98
vinyl acetate	9.19	0.0	26.2	0	26
tetrahydrofuran	9.41	1.0	17.7	18	0
1-hexene	9.44	0.08	27.0	2.2	25
3,3-dimethyl-1-butene	9.45	0.0	7.47	0	7.5
trichloroethylene	9.47	0.0	5.42	0	5.4
trans-1,2-dichloroethylene	9.66	0.0	2.41	0	2.4
allyl alcohol	9.67	0.19	20.9	4.0	17
crotonaldehyde	10.1		12.5		
methacrylonitrile	10.34	0.0	3.65	0	3.7
crotonic acid	10.6	0.04	3.51	0.14	3.4
1,2-dimethylcyclohexene		0.51	570	291	279
3-methyl-2-buten-1-ol		0.17	180	32	150
2-bromo-2-butene		0.02	100	2.0	98
3-chloro-1-butene			4.0		
decafluorobenzhydrol			0.255		

^a k_H is the calculated rate constant for hydrogen abstraction and k_π the rate constant for addition.

TABLE 2: Rate Constants and Quantum Yields of Ketyl Radical Formation for Reactions of ³DFB with Alkenes in Carbon Tetrachloride

alkene	Φ_K	$k_r \times 10^{-7}$, L mol ⁻¹ s ⁻¹	$k_H \times 10^{-7}$, L mol ⁻¹ s ⁻¹	$k_\pi \times 10^{-7}$, L mol ⁻¹ s ⁻¹
2-methyl-3-ethyl-2-pentene	0.30	204	61	140
2,3-dimethyl-2-butene	0.25	249	62	190
bicyclo[2.2.1]hepta-2,5-diene	0.00	269	0	270
1-methylcyclopentene	0.25	206	52	160
2-methoxypropene	0.0	214	0	210
1-methylcyclohexene	0.27	260	70	190
2-methyl-2-butene	0.05	148	7.4	140
ethyl vinyl ether	0.0	124	0	120
1,4-cyclohexadiene	0.17	298	5	250
furan	0.0	177	0	180
2,4,4-trimethyl-1-pentene	0.02	118	1.8	120
cyclohexene	0.07	169	12	160
cis-3-hexene	0.06	101	5.7	95
trans-2-hexene	0.10	89.3	8.5	81
trans-4-methyl-2-pentene	0.08	62.7	5.0	58
cyclopentene	0.10	164	16	150
vinyl acetate	0.0	30.6	0	31
tetrahydrofuran	1.0	33.6	34	0
1-hexene		54.8		
3,3-dimethyl-1-butene	0.0	9.29	0	9.3
trichloroethylene	0.0	6.63	0	6.6
trans-1,2-dichloroethylene	0.02	1.92	0	1.9
crotonaldehyde			73.1	
methacrylonitrile	0.0	4.53	0	4.7
crotonic acid	0.03	5.14	0.18	5.0
1,2-dimethylcyclohexene	0.42	266	110	150
3-methyl-2-buten-1-ol	0.15	185	28	160
2-bromo-2-butene	0.12	81	9.7	71
3-chloro-1-butene	0.05	4.0	0.17	3.4

^a k_H is the calculated rate constant for hydrogen abstraction and k_π the rate constant for addition.

The slopes of the IP vs log k plots for reactions involving triplet benzophenone, biacetyl, and benzil with alkenes increase

with an increase in the reduction potentials of the ketones. For example, the slope is -1.5 eV^{-1} for benzophenone, and for

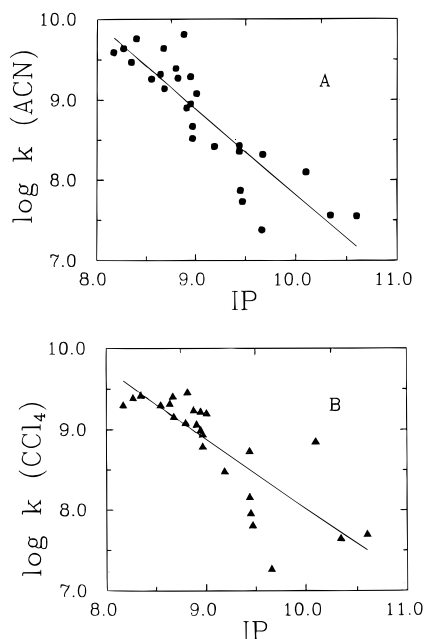


Figure 1. Plot of $\log k_r$ versus IP, in (A) acetonitrile, (B) carbon tetrachloride.

biacetyl and benzil the slopes are -1.7 eV^{-1} in the endothermic region and -5.8 eV^{-1} in the exothermic region, which is in line with their ground state reduction potentials of -2.16 , -1.66 , and -1.5 V , respectively.¹⁰ In view of this example and the results normally expected from a reaction involving charge transfer, the slope expected for reaction of ³DFB, which has $E_{1/2} = -1.21 \text{ V}$,⁴² is much greater than experimentally observed, -1.1 eV^{-1} .

A possible reason for the less than expected slope is the high rate constant for hydrogen abstraction by ³DFB, which is 10 – 40 times higher than for ³BP, which in turn is 10^2 – 10^3 times faster than for triplet biacetyl and benzil.^{4,42,43} It is possible that, for ³DFB, direct hydrogen abstraction competes with exciplex formation for alkenes with high ionization potentials. To investigate this possibility, we have estimated the separation of the total rate constant, k_r , into the contribution from the hydrogen-abstraction pathway, k_H , and the 1,4-biradical pathway, k_π , by determining the quantum yield, Φ_K , for the production of the ketyl radical, which is formed in the hydrogen-abstraction reaction. If we assume that the direct formation of ground-state reactants from the complex is not important ($k_q \ll k_H + k_\pi$), then

$$k_r = k_H + k_\pi$$

and

$$\Phi_K = k_H/k_r$$

The quantum yields were determined relative to the quantum yield for ketyl radical formation in the reaction of ³DFB with tetrahydrofuran by measuring the absorbance of the ketyl radical at 530 nm . By assuming that the quenching of ³DFB by tetrahydrofuran proceeds exclusively via hydrogen abstraction, or $\Phi_K^{\text{THF}} = 1$, we can convert these relative quantum yields to absolute values and derive values of k_H and k_π . These relative values of Φ_K are included in Tables 1 and 2 for acetonitrile and carbon tetrachloride, respectively, and the derived values of k_H and k_π in Tables 1 and 2.

The dependence of $\log k_\pi$ on IP is presented in Figure 2. The slopes are -1.0 and -0.94 eV^{-1} in acetonitrile and carbon tetrachloride, respectively, and are very similar to the slopes

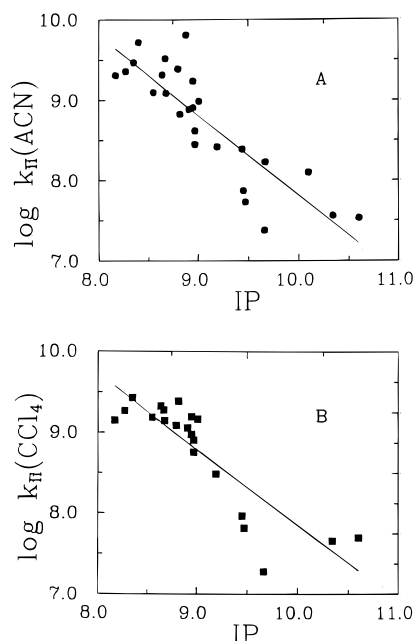


Figure 2. Plot of $\log k_\pi$ versus IP, in (A) acetonitrile, (B) carbon tetrachloride.

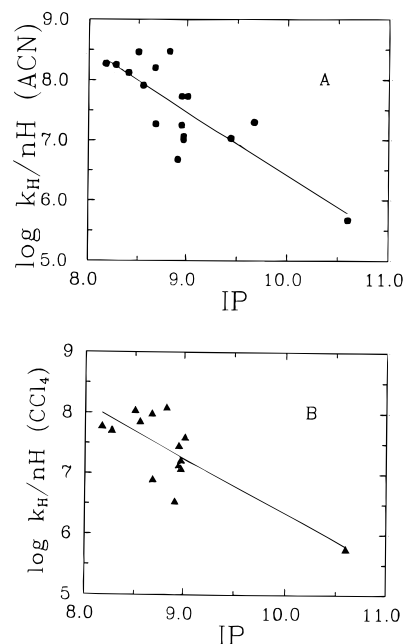


Figure 3. Plot of $\log k_H$ versus IP, in (A) acetonitrile, (B) carbon tetrachloride.

obtained for the overall rate constants. The plots of $\log k_H/nH$ (Figure 3), where nH is the number of activated hydrogens, against IP are much more limited and strongly weighted by a single point at high IP. Nevertheless, the same trend is apparent. The slopes obtained are -1.05 and -0.90 eV^{-1} for acetonitrile and carbon tetrachloride as solvents, respectively. These values are very similar to those obtained from the dependence of $\log k_r$ and $\log k_\pi$ on IP. These results suggest that the dependence of both $\log k_H$ and $\log k_\pi$ on the IP (of the alkenes) are of the same magnitude and direction as that of k_r , the overall rate constant.

Evidence that both k_H and k_π proceed via similar mechanism in polar acetonitrile and nonpolar carbon tetrachloride as solvents is indicated by the linear relationship between the rate constants, as demonstrated by the log–log plots of k_r , k_H , and k_π . These all yield slopes of 1.1 , indicating that the mechanism does not

change with the properties of the solvent. This is in contrast to reactions involving complete charge transfer, where the ratio of the rate constants measured in polar and nonpolar solvents are typically about 13.^{4,24,38}

One possible mechanism for the abstraction of the α -hydrogen atoms involves the addition of the ³DFB to the alkene to form the 1,4-biradical, with the subsequent abstraction of the hydrogen to yield the ketyl radical in competition with ring closure. This would be similar to the mechanism for the reaction of NO₂ with alkenes,^{50,51} except in that case the ring closure product is not stable. For the perpendicular addition of the ³DFB to an alkene, however, this mechanism is less likely since orbital correlations predict the formation of a carbon–oxygen bonded biradical,³³ and it is unlikely that abstraction by the carbon-centered radical site would be facile. This then further supports the existence of a precursor complex, the exciplex, from which the abstraction takes place. The similarity between the kinetic results for the addition and the abstraction reactions would appear to rule out an independent abstraction pathway.

Conclusion

The rate constants for the reactions of ³DFB with alkenes depend strongly on the electronic properties of the alkene. The dependence of the rate constant on the ionization potential and the weak dependence on steric effects are consistent with the formation of an excited complex as the first step in the reaction. The dependence of Φ_K on IP but not on the absolute rate constant suggests that hydrogen abstraction proceeds also via this complex.

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