Rate Studies of Aromatic Triplet Carbonyls with Hydrocarbons

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Abstract: The rate constants, activation energies, and A factors for the interaction of triplet benzophenone, acetophenone, and benzaldehyde with a series of hydrocarbons have been determined and the data compared with the corresponding reactions of alkyl and alkoxy radicals. The difference in reactivities for hydrogen abstraction from alkanes is attributed mainly to variations in the activation energy. The A factors are remarkably constant ($10^{7.8}$ M^{-1} sec^{-1}). While triplet benzaldehyde is about six times more reactive than triplet benzophenone for hydrogen abstraction from an aliphatic hydrocarbon such as cyclohexane, its reactivity toward an aromatic hydrocarbon such as benzene is 800 times greater than that of triplet benzophenone. The negative activation energies found in the case of aromatic hydrocarbon interactions with triplet benzaldehyde suggest that there is an equilibrium between benzaldehyde triplets and a complex.

In recent years, the reactivities of triplet aromatic ketones have been actively studied. The free-radical character of triplet carbonyls is evidenced by their ability to abstract hydrogen from various hydrocarbon substrates, and their reactivity patterns have been compared to alkoxy radicals.[1,2] The interaction of triplet carbonyls with aromatic substrates is more complicated, and various types of complex formation have been suggested.[3-8] The amount of absolute rate constant data for the reaction of triplet ketones with hydrocarbons is neither extensive or systematic. Furthermore, there are no Arrhenius parameters. We felt it would be useful to have such information to establish patterns so that the rate constant for hydrogen abstraction from any alkane could be predicted with some confidence. We also felt that such information would be of interest because hydrogen abstraction is a class of reactions amenable to fairly detailed theoretical analysis

and because the data could shed more light on the nature of triplet carbonyl reactivity.

Experimental Section

Materials. The solvents (acetonitrile, benzene, and isooctane) were all Spectrograde. They were carefully distilled and dried before use and then checked for lack of emission in the region 400–600 nm. Hydrocarbons were the best grades commercially available: Matheson, Chemical Samples, and Phillips Petroleum. Nevertheless, it was found that most of the hydrocarbons contained trace (~0.2%) quantities of olefins. In agreement with previous studies,[9-12] we found that olefins had reactivities which were often over 10^3 times greater than the reactivities of the hydrocarbons used in this study. Therefore, it was necessary to ensure that olefin impurities were reduced to less than 0.005%. This was done by repeatedly washing with concentrated sulfuric acid followed by passage through basic alumina. Finally, the purity of the hydrocarbon was checked by gas chromatographic analysis using a silver nitrate column selective for olefins.[13] Benzophenone, acetophenone, and benzaldehyde were all Fisher Certified Reagent grade. The benzophenone was recrystallized twice from ethanol followed by vacuum sublimation. The acetophenone and benzaldehyde were distilled under vacuum on a good distillation column, middle cuts being employed.

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Apparatus. Two methods were used to determine the rate constant for triplet interaction with hydrocarbons (k_{ir}).

Method 1. Direct measurement of the variation in triplet lifetime as hydrocarbon, RH, is added

$$1/\tau_{RH} = 1/\tau + k_{ir}[RH] \tag{1}$$

where τ and τ_{RH} are the lifetimes in the absence and presence of RH, respectively. A general description of the lifetime equipment has previously been given.[14] Ordinarily, τ_{RH} was measured at four different RH concentrations to determine the Stern-Volmer slope, k_{ir}.

Method 2. Measurement of steady-state emission intensities in the absence, $I(0)$, and in the presence of varying concentrations of RH, $I(RH)$.

$$\frac{I(0)}{I(RH)} = 1 + \tau k_{ir}[RH] \tag{2}$$

The emission spectra of benzophenone and acetophenone at room temperature have already been reported.[15] Benzaldehyde phosphorescence in isooctane and acetonitrile closely resembles that obtained in the glass[16] and in the gas phase[17-19] except for a blurring of fine structure in the liquid phase. The positions of the vibronic maxima in the emission spectra of benzophenone, acetophenone, and benzaldehyde are not shifted within our experimental resolution (1 mμ) in going from isooctane to acetonitrile. Likewise, the maxima for benzaldehyde and acetophenone are unaffected in going from the liquid to the gas phase. This indicates that the $^3n,\pi^*$ energies are not significantly altered by change of phase or by the solvents employed. While methods 1 and 2 gave identical values of k_{ir} within experimental error, most data in this report were obtained using the first method.

In determining the quantum yields the experimental emission spectra were corrected by the standard method, allowing for the response of the photomultiplier and the sensitivity of the emission monochromator as a function of λ.[20] Quinine sulfate was used as the standard.[21,22]

Solvents. The ideal solvent must readily dissolve the reagents but must not react with the triplet carbonyls. The hydrocarbons and the carbonyls are quite soluble in benzene and isooctane; however, the high reactivity of benzaldehyde triplets with these solvents precluded their use (*vide infra*). Fluorocarbons are chemically inert[23] but most common reagents are quite insoluble in these solvents. Acetonitrile was the solvent most commonly used in this work. The emission lifetimes were quite long in acetonitrile indicating its chemical inertness toward the triplets. Typical lifetimes were benzophenone $(5 \times 10^{-3} M) = 104 \mu$sec, acetophenone $(1 \times 10^{-4} M) = 130 \mu$sec, and benzaldehyde $(1 \times 10^{-4} M) = 17 \mu$sec. A long lifetime allowed the study of quenchers with low reactivities without going to quencher concentrations greater than $10^{-1} M$. Benzophenone, acetophenone, and benzaldehyde undergo self-quenching. The measured self-quenching constants were, respectively, 7.5×10^5, 189×10^5, and $670 \times 10^5 M^{-1} \sec^{-1}$ in acetonitrile. In benzene the rate constants were 2.5×10^5 and $8.2 \times 10^5 M^{-1} \sec^{-1}$ for benzophenone and acetophenone. The value for benzophenone in benzene agrees well with the results obtained by Schuster and Weil.[24] The τ value in each experiment, see eq 1, includes the self-quenching term. This does not affect the determination of k_{ir}, since the carbonyl concentration is held constant so that τ is also constant.

In typical day to day operation the lifetime in the absence of quencher could vary by 15%. This was certainly not due to the degassing technique or to our measuring capability but was probably due to trace contaminants in the solvent. This variation in τ, however, did not affect our results since we always measured the lifetimes before and after the addition of the hydrocarbon.

Activation Energies. To carry out activation energy determinations the emission cell compartment was thermostated over the range -30 to $+70°$. The lower and upper limits were set by the freezing point $(-45°)$ and boiling point $(+81°)$ of acetonitrile. Typically, τ was determined at eight temperatures. A hydrocarbon was added and τ_{RH} determined at the same eight temperatures. The values of k_{ir} at these temperatures were then obtained using eq 1. Because of the very low activation energies, τ and τ_{RH} did not vary dramatically over the temperature range employed. We found that a typical 2.5% deviation in τ_{RH} and τ resulted in a 0.3 kcal mol^{-1} variation in the activation energy (E_{ir}) and a 0.2 unit variation in log A.

Results and Discussion

(1) Effect of Solvent and Phase. Solvent effects can be important if they change the relative $^3n,\pi^*$ and $^3\pi,\pi^*$ spacings or if they affect the energy of the lowest triplet.[25-27] Although acetonitrile has a high dielectric constant (ϵ 38), it cannot form hydrogen bonds, and as we have pointed out in the Experimental Section, we could observe no change in the positions of the phosphorescence vibronic maxima in going from isooctane to acetonitrile solvents. From the data in ref 15, radiative triplet lifetimes, $\tau_0 = \tau/\varphi_{em}$, for benzophenone and acetophenone in isooctane are both estimated to be 5.0×10^{-3} sec. Similar values were obtained in acetonitrile. These values are in good agreement with those reported for low-temperature glasses, viz., 6.35 and 3.71 $\times 10^{-3}$ sec, respectively.[28] Because of the short lifetime of triplet benzaldehyde in isooctane we could not obtain a good value of τ_0 in this solvent, but in acetonitrile the value was 3.6×10^{-3} sec. In the gas phase the value was 2.5×10^{-3} sec.[29] In this case the glass value is given as 3.1×10^{-3} sec.[28] The similarity in all the τ_0 values and the insensitivity to solvent or to phase indicates that the possible complications mentioned at the beginning of this section are absent under the conditions of this study.

It has been shown that in simple cases where there are no strong solvation effects associated with either the reactants or the transition state the rate of a reaction should be insensitive to the phase or to the nature of the solvent.[30] The results in Table I show that the rates of

Table I. Interaction Rate Constants of Triplet Acetophenone with Cyclohexane at 25°

Phase	Solvent	$10^{-5}k_{ir}, M^{-1}$ sec^{-1}
Liquid	Benzene (ϵ 2.3)	4.7
Liquid	Acetonitrile (ϵ 38)	3.9
Gas		4.8

hydrogen abstraction by triplet acetophenone from cyclohexane are indeed insensitive to both phase and solvent polarity. The absence of strong solvation

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Table II. Interaction Rate Constants of Triplet Aromatic Carbonyls with Selected Hydrocarbons

Hydrocarbon	$10^{-5}k_{ir}$,[a] M^{-1} sec^{-1}		
	Ph_2CO	$PhCOCH_3$	$PhCHO$
Cyclohexane	7.2	3.9	41
Isooctane	1.0 (0.66)	0.58 (0.82)	15
Benzene	0.27 (0.14)	0.25 (0.25)	220
Toluene	3.8	1.9	930

[a] The temperature is 25°; the values not in parentheses were obtained using eq 1 and dilute solutions of the hydrocarbons in acetonitrile. The values in parentheses were obtained when the hydrocarbons were themselves the solvents, see text.

effects for hydrogen abstraction is also shown by another experiment. If τ_{RH} is sufficiently short compared to τ, then eq 1 becomes $k_{ir} = 1/[RH]\tau_{RH}$. The lifetimes of triplet benzophenone in isooctane and benzene at room temperature are 2.5 and 6.5 $\times$ 10^{-6} sec, respectively, while the corresponding lifetimes for triplet acetophenone are 2.0 and 3.5 $\times$ 10^{-6} sec.[11] These data together with the above equation yield the values of k_{ir} given in parentheses in Table II. There is fairly good agreement with the values obtained for dilute acetonitrile solutions using eq 1.

(2) Activation Energies. For hydrogen abstraction by a triplet (T*) we have

$$T^* + RH \xrightarrow{k_{ir}} TH\cdot + \cdot R \qquad (3)$$
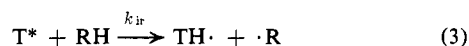
If $k_d \approx 4\pi ND/1000$ is the second-order diffusion constant,[31] k_a is the first-order rate constant for abstraction by $\{T^*, RH\}$ encounter pairs, and $k_{-d} \approx 6D/\sigma^2$ is the first-order constant for diffusion of T* and RH out of the solvent cage,[32] then $k_{ir} = k_d/(k_a/k_a + k_{-d})$. Thus

$$k_{ir} \approx \frac{k_d}{k_{-d}} k_a \qquad (4)$$

when $k_{ir} \ll k_d$. Since the temperature coefficients of k_d and k_{-d}, and hence the activation energies E_d and E_{-d}, should be the same, it is apparent from eq 4 that the activation energy associated with k_{ir} stems solely from the activation energy associated with the abstraction process (E_a) and does not incorporate the activation energy of diffusion. The experimental values of E_a will be discussed later. E_d can be readily determined by studying the temperature dependence of a diffusion-controlled reaction ($k_{ir} = k_d$). The reactions chosen were the quenching of acetophenone and benzophenone triplet by naphthalene.[33] The quenching was studied in both isooctane and benzene as solvent. The activation energies in benzene ($\sim$3.1 kcal mol^{-1}) and in isooctane ($\sim$2.3 kcal mol^{-1}) were, within experimental error, the same as obtained by plotting log (T/η) vs. $1/T$ where η is the solvent viscosity and T the absolute temperature. This is as would be expected by simple theory.[28] For acetonitrile such a viscosity plot[34a] yields $E_d = 2.1$ kcal mol^{-1}.

(3) Hydrogen Abstraction from Aliphatic Hydrocarbon by Triplet Benzophenone. In the case of simple saturated hydrocarbons there can be little doubt that the interaction rate constants (k_{ir}) which were determined using eq 1 or 2 in fact refer to hydrogen abstraction by the triplet. Several such rate constants for reaction with benzophenone triplets are shown in Table III.

Table III. Absolute Rate Constants for Reaction of Triplet Benzophenone with Hydrocarbons

Hydrocarbon	$10^{-5}k_{ir}$,[a] M^{-1} sec^{-1}
2,2-Dimethylpropane	0.43
2,2,3,3-Tetramethylbutane	0.31
2-Methylpropane	5.7
2,3-Dimethylbutane	9.3
Cyclohexane	7.2
2,2,4,4-Tetramethylpentane	1.7
2,2,4-Trimethylpentane (isooctane)	1.7

[a] The temperature is 25°; the solvent is acetonitrile.

In studying such hydrogen abstractions it is common practice to interpret the experimentally observed overall rate constants in terms of rate constants per hydrogen atom (primary, secondary, and tertiary).[35-37] In general, when the number of abstractable hydrogens of a given type (primary, secondary, and tertiary) increases, the observed overall rate constant increases proportionally so that the rate constant per hydrogen remains essentially constant. It might therefore be expected that this change would be reflected in a varying A factor.[37,38] The most extensive data exist for methyl radicals,[38,39] and in this case abstraction from a series of hydrocarbons with a given type of hydrogen yields an essentially constant A factor and there is no correlation with the number of abstractable hydrogens. It is also observed experimentally that the difference in reactivity between a primary, secondary, and tertiary hydrogen stems from a varying activation energy.[38]

In Table IV we have gathered together rate constants for abstraction of primary, secondary, and tertiary hydrogen by benzophenone triplets as determined from the first six entries in Table III. The data for toluene, Table II, have also been incorporated as well as the data of Saltiel[5] and Dedinas[6] for benzene. The trend $k_{tert} > k_{sec} > k_{prim}$ can clearly be seen. The variation for triplet benzophenone agrees excellently with the relative values obtained by Walling and Gibian[1] who used chemical product analyses. The relative intramolecular reactivities for hydrogen abstraction by the triplet benzoyl group as described by Wagner[40] also agree with those found for triplet benzophenone.

The Arrhenius parameters are presented in Table V. The constancy in the A factors will be noted and the

(31) N is Avogadro's number and D is the diffusion coefficient: J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970, p 312.

(32) P. J. Wagner and I. Kochever, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

(33) W. D. K. Clark, A. D. Litt, and C. Steel, *Chem. Commun.*, 1087 (1969).

(34) (a) Data taken from "Handbook of Chemistry and Physics," 53rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1973, pp F-37 and F-189; (b) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

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Table IV. Relative Rate Constants per Hydrogen for Hydrogen Abstraction from Hydrocarbons by Methyl Radicals, *tert*-Butoxy Radicals, Benzophenone, and Benzoyl Triplets

Type of R–H bond broken	—Methyl radical— Gas[a]	Soln[b]	*tert*-Butoxy radical Soln[c]	Soln[d]	Triplet benzophenone Soln[d]	Soln[e]	Triplet benzoyl Soln[h]
Primary	1	1	1	1	<1	1	1
Secondary	7.0	4.3	7	12		40	24
Tertiary	50	46	28	44	300	300	180
Secondary cyclohexyl	5.7	3.1	20	15	50	35	
Primary benzylic	15	10	12	10		74	80
Benzene C–H	0.57		0.03			0.016[f]	
						0.0018[g]	

[a] Absolute values at 182° in units of M^{-1} sec^{-1} can be obtained by multiplying by 0.3 × 10³, ref 35. [b] Relative values at 110°, ref 36. [c] Relative values at 135°: A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Amer. Chem. Soc.*, **78**, 1190 (1956). [d] Relative values at 40°, ref 1 and C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961). [e] Absolute values at 25° in units of M^{-1} sec^{-1} can be obtained by multiplying by 0.17 × 10⁴, this work except for benzene C–H. [f] Reference 6. [g] Reference 5. [h] Reference 40.
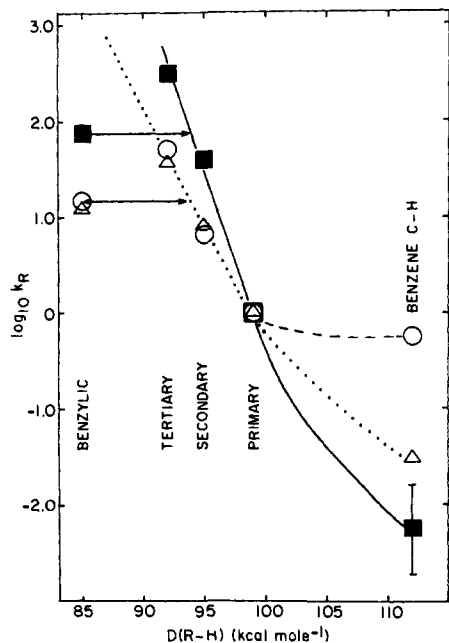

Figure 1. Relative rate constants per hydrogen, k_R, as a function of the bond dissociation energy of the breaking bond. Data from Table IV and ref 34: methyl radicals (○); *tert*-butoxy radicals (△); triplet benzophenone (■).

Table V. Arrhenius Parameters for Hydrogen Abstraction from Selected Hydrocarbons by Triplet Benzophenone

Hydrocarbon	Type of hydrogen abstracted	Log A, M^{-1} sec^{-1}	E_a, kcal mol^{-1}
2,2,3,3-Tetramethyl-butane	Primary	7.7	4.4
Cyclohexane	Secondary	8.0	2.8
2,3-Dimethylbutane	Tertiary	7.5	2.2
Toluene	Primary benzylic	7.6	2.5

decrease in the activation energy in going from primary to secondary to tertiary is clear. In Figure 1 the rate constants from Table IV have been plotted as a function of the dissociation energy of the breaking bond. It will be seen that triplet benzophenone is definitely more selective than either methyl or *tert*-butoxy radicals. The deviation from the straight line for the benzene data is more pronounced for the less reactive methyl radical than for the more reactive *tert*-butoxy radical and benzophenone triplet. Although the change in activa-

tion energy in going from primary to tertiary hydrogens for methyl radicals and benzophenone triplets is quite similar,[41] the percentage change is greater for the latter. Thus, benzophenone triplets are both more reactive and more selective than methyl radicals.

The relative rate constants for benzylic hydrogen (toluene) are less than would be expected from the bond dissociation energy, and it is interesting to note that the deviations are the same for methyl, *tert*-butoxy, and triplet benzophenone. An excellent linear Polanyi plot,[38,42] $E_a = 0.32D(R–H) − 26.9$, can be obtained by graphing the experimental activation energies for the first three entries in Table V. Toluene lies off this line, the activation energy being higher than expected from the $D(R–H)$ value. This is consistent with the low reactivity indicated in Figure 1.

In the above discussion reference to the isooctane data (Table III) has been omitted. This hydrocarbon was investigated because much of our early work was carried out using this solvent. Although it has a tertiary hydrogen, significantly lower rates were obtained for isooctane than for other hydrocarbons with tertiary hydrogen. A model shows that the tertiary hydrogen is effectively shielded by a methyl group, which presumably prevents attack by a bulky reagent such as triplet benzophenone.

(4) Comparisons between Aromatic Triplet Carbonyls. (a) Alkanes. The data in Table II show that in its reactions with saturated hydrocarbons, triplet acetophenone is slightly less reactive than triplet benzophenone, while triplet benzaldehyde is about six times more reactive than the latter. This increased reactivity is associated with a drop in activation energy (Table VI). There is apparently no significant variation in the A factors.

There have been several attempts to systematize the data for hydrogen abstraction reactions of the type

$$R'· + H–R \xrightarrow{k} R'–H + ·R \qquad (5)$$

$$\Delta H = D(R–H) − D(R'–H)$$
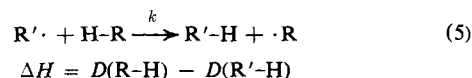
The familiar Polanyi relation relates the activation energy to $D(R–H)$ for constant R'· and a series of substrates RH.[38] This correlation for triplet benzophenone has already been discussed. However, trends in k as R'· is varied and RH is held constant have been less

(41) For CH₃·, E_a for 2,2,3,3-tetramethylbutane is 9.5 kcal mol^{-1} and E_a for 2,3-dimethylbutane is 7.8 kcal mol^{-1}; see ref 35.
(42) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

Table VI. Arrhenius Parameters for the Interaction Rate Constants of Benzophenone, Acetophenone, and Benzaldehyde with Selected Hydrocarbons

Triplet	Hydro-carbon	$k_{ir} \times 10^{-5}$ (25°), M^{-1} sec^{-1}	Log A, M^{-1} sec^{-1}	E_{ir}, kcal mol^{-1}
Benzophenone	Benzene	0.27	6.8	+3.3
	Toluene	4.1	7.6 (9.1)^a	+2.5 (4.16)^a
	Cyclohexane	7.5	8.0 (10.8)^a	+2.8 (7.6)^a
	Isooctane	1.0	7.8	+3.9
Acetophenone	Benzene	0.25	7.2	+3.7
	Toluene	2.2	7.8 (8.7)^a	+3.3 (3.09)^a
	Cyclohexane	3.5	8.0 (10.3)^a	+3.3 (5.66)^a
	Isooctane	0.50	7.7	+4.1
Benzaldehyde	Benzene	220	6.7	−0.7
	Toluene	1000	6.3	−2.4
	Cyclohexane	41	6.8	+0.3
	Isooctane	15	7.4	+1.7

^{a} Predicted from ref 49; all other entries are this work.

successfully explained. BEBO (bond energy bond order) calculations, for example, indicate that the CF$_3$· and CH$_3$· radicals should have similar reactivities,[43] since D(CH$_3$–H) and D(CF$_3$–H) are similar. Nevertheless, CF$_3$· radicals react about 300 times more rapidly than CH$_3$· radicals.[44] Also, from Table VII it will

Table VII. Arrhenius Factors for R'· + H-C(CH$_3$)$_3$ → R'-H + ·C(CH$_3$)$_3$ (k_a)

Radical	Phase	D-(R'-H),^{a} kcal mol^{-1}	Log k_{25}, M^{-1} sec^{-1}	Log A, M^{-1} sec^{-1}	E_a, kcal mol^{-1}	Ref
CH$_3$·	Gas	104	2.3	7.8	7.5	39
CH$_3$O·	Gas	104	4.9	7.9	4.1	d
tert-(CH$_3$)$_3$CO·	Gas	104	4.9	7.8	4.0	e
^{3}(C$_6$H$_5$)$_2$CO*	Liquid		5.8^b	(7.5)^c	(2.4)^c	

^{a} Reference 29. ^{b} This work for isobutane. ^{c} This work, estimated from E_a and A values for 2,3-dimethylbutane which has two tertiary hydrogens. See Tables III and V. ^{d} T. Bercés and A. F. Trotman-Dickenson, J. Chem. Soc., 348 (1961). ^{e} G. R. McMillan, J. Amer. Chem. Soc., 82, 2422 (1960).

be seen that although D(R'-H) does not vary significantly in going from methyl to tert-butoxy, there is, nevertheless, a 400-fold variation in rate constant which is due to an activation energy decrease. The remarkable constancy in the A factors throughout the series will be noted.

The greater electronegativity of the oxygen atom can explain the lower activation energy for alkoxy radicals, because the outward facing lobe of the orbital associated with the unpaired electron is contracted or displaced toward the center of the group. Thus, closer approach of the attacking radical may be possible before electron repulsion effects become significant. Electron withdrawing groups on the radical may also "shrink" the outward lobe by inductive effects, similarily lowering the activation energy.

The higher rate constant for hydrogen abstraction by triplet benzophenone is associated again with a decrease in activation energy, while the A factor remains almost unchanged. It is interesting to note that recent

(43) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966.
(44) (a) R. E. Dodd and J. W. Smith, J. Chem. Soc., 1465 (1957); (b) P. B. Ayscough and E. W. R. Steacie, Can. J. Chem., 34, 103 (1956).

studies[45–47] indicate that the n orbital of aromatic ketones is significantly delocalized into the ring. This has the effect of displacing the free electron toward the center of mass. From the above one might expect a relationship between the reactivity and the electrophilicity of the attacking species. As measured by their reactivities with cyclohexane, triplet α-trifluoroacetophenone[8] is seven times more reactive than benzophenone (k_{ir} = 47 × 10^5 and 7.2 × 10^5 M^{-1} sec^{-1}, respectively). Thus, we have the reactivity order triplet α-trifluoroacetophenone > triplet benzophenone > tert-butoxy radicals. The corresponding Hammett ρ values for reaction with substituted toluenes are −2.0,[8] −1.16,[1] and −0.83,[48] respectively.

In triplet carbonyl reactions the process corresponding to eq 5 is

$$^3R_2'CO^* + H\text{-}R \xrightarrow{k_{ir}} R_2'\dot{C}\text{-}OH + \cdot R \qquad (6)$$
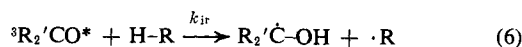
$$\Delta H = D(R\text{-}H) - \{E_T - E_\pi + E(O\text{-}H)\}$$

where $E_\pi = E(C=O) - E(C-O)$ is the carbonyl "π-bond energy." The trend in activation energy with D(R–H) for abstraction by triplet benzophenone of primary, secondary, and tertiary hydrogen has already been discussed. The term $\{E_T - E_\pi + E(O\text{-}H)\}$ plays the role of D(R'–H), the strength of the forming bond, in eq 5. Previtali and Scaiano[49] carried out a BEBO calculation for hydrogen abstraction by triplet benzophenone and acetophenone. They took E_π and E(O–H) to be the same for both carbonyls. Thus, for attack on a given hydrogen, D(R–H) constant, they predicted a relationship between reactivity and E_T, since the BEBO method demands a correlation between the rate constant and ΔH. The triplet energies for benzophenone, acetophenone, and benzaldehyde are respectively 69.3, 73.6, and 71.3 kcal mol^{-1}.[28] Obviously, the rate constants in Table VI show no correlation with E_T. This is perhaps not surprising since as shown above in the general case of radical reactions, eq 5 and Table VII, the correlation with D(R'–H) is also poor. Previtali and Scaiano used the value of E_π estimated by Walsh and Benson[50] for acetone (74.6 kcal mol^{-1}). This does not take into account the benzylic resonance that should be present in aromatic ketyl radicals. Other estimates of E_π for aromatic carbonyls are considerably lower.[51] A resonance stabilization of 9 kcal mol^{-1} for triplet benzophenone, and 5 kcal mol^{-1} for triplet acetophenone would make their predicted reactivities similar to that for triplet acetone. This is what is observed experimentally; the k_{ir} for triplet acetone and cyclohexane is 3.2 ± 0.5 × 10^5 M^{-1} sec^{-1},[52] while the corresponding constant for triplet acetophenone is 3.7 × 10^5 M^{-1} sec^{-1} (Table VI).

(b) Aromatic Hydrocarbons. Although the k_{ir}'s of benzene and toluene with triplet benzophenone and

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triplet acetophenone are comparable, their k_{ir}'s with triplet benzaldehyde are very much larger than might have been expected from consideration of the aliphatic hydrocarbon data. Thus, triplet benzaldehyde reacts six times more rapidly with cyclohexane but 800 times more rapidly with benzene than does triplet benzophenone.

It has been suggested that triplet benzophenone forms a complex with benzene. It was first suggested that the complex was a diradical adduct.[3,4] More recently, a more general type of complex possibly involving charge-transfer stabilization has been invoked. For the interaction of triplet benzophenone with substituted benzenes, the data of Schuster, et al.,[7] indicated that the aromatic moiety becomes negatively charged, while the data of Wagner and Leavitt[8] indicated that for trifluoroacetophenone it is the carbonyl which becomes negatively charged. The k_{ir}'s for triplet acetophenone, benzophenone, and α-trifluoroacetophenone[8] with benzene are, respectively, 0.25×10^5, 0.27×10^5, and 9×10^5 M^{-1} sec^{-1}. If the rate of complex formation depended on the fractional charge-transfer character of the complex and if the carbonyl were the electron acceptor, then the rates might be expected to be a function of (EA + E_T), the sum of the electron affinity and the triplet energy of the carbonyl.[53,54] The values of (EA + E_T) for the carbonyls given above are proportional to 1.13, 1.16, and 1.65 eV,[55] and these do increase in the expected order. However, in the case of benzaldehyde, which has the highest k_{ir} with benzene (220×10^5 M^{-1} sec^{-1}), (EA + E_T) is proportional to 1.14 eV. If the carbonyl were positively charged in the complex, then k_{ir} should increase with decreasing value of (IP − E_T), where IP is the ionization potential of the carbonyl. For acetophenone, benzophenone, and benzaldehyde (IP − E_T) is 6.46, 6.45, and 6.51 eV.[55] Again there is no trend with k_{ir}.

Recently, Loufty and Yip[58] have suggested that the role of the charge-transfer state may be to interact by configuration interaction with the zero-order locally

excited state (ketone, ^{3}benzene*) resulting in a lowering of the energy of the latter so that better exchange interaction may occur between it and the other locally excited state (^{3}ketone*, benzene). However, the data in ref 55 and 58 show that the energies for the three zero-order states (ketone$^-$, benzene$^+$), (ketone, ^{3}benzene*), and (^{3}ketone*, benzene) are quite similar for both benzophenone and benzaldehyde, although the rate constants differ by three orders of magnitude. Indeed triplet benzaldehyde reacts with benzene an order of magnitude more rapidly than does triplet acetone, although the two zero-order locally excited states of the latter lie significantly closer together than those of benzaldehyde.

Whatever the detailed mechanism of the quenching, the data for benzene in Table VI show that the activation energy for the quenching channel is much lower than the activation energy for hydrogen abstraction from benzene which we would estimate from a Polanyi plot. Thus, hydrogen abstraction cannot compete with the other quenching channel(s).

Toluene has much more readily abstractable hydrogens than does benzene and as shown above its reactivity with triplet benzophenone and acetophenone is what one would expect for direct hydrogen abstraction. However, this is not so in the case of benzaldehyde (Tables II and VI). The extremely high-interaction constants for triplet benzaldehyde with both benzene and toluene have already been mentioned. These constants are even higher than the corresponding constants for α-trifluoroacetophenone. It is significant that the experimental activation energies are negative. Negative activation energies have been postulated in systems involving the reversible formation of an excimer or exciplex.[59-61] In the case of benzaldehyde the analogous scheme is

$$^3PhCHO^* + Ar \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} PhCHO\cdots Ar \xrightarrow{k_q} quenching$$
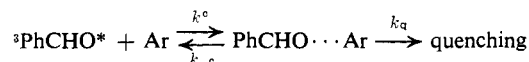
The overall rate constant k_{ir} equals $(k_c/k_{-c})k_q$ if $k_{-c} > k_q$, so that $E_{ir} = (-\Delta H_c + E_q)$ where ΔH_c is the binding energy of the complex. Negative activation energies are then obtained when $\Delta H_c > E_q$.

It should be noted that when hydrogen abstraction is the predominant reaction pathway the A factors are close to $10^{7.8}$ M^{-1} sec^{-1}, but where complex formation is dominant, the A factors seem to be lower.

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|	Benzophenone[57]	Acetophenone[57]	α-Trifluoroacetophenone[8]	Benzaldehyde[57]
$\epsilon(A^-/A)$, V	−1.84	−2.06	−1.42	−1.95
IP, V	9.45	9.65		9.60
E_T, V	3.00	3.19	3.07	3.90

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