to λ, it is found that the best λ for either $\varphi = 0$ or $\varphi = 60°$ is 1.03. The minimized energies are −116.237952 and −116.236659.

The dipole moment of the most stable conformation of propylene was calculated to be 0.089 D with the (5,3,3) basis and 0.058 D with the (5,2,2) set. The experimental value[31] is 0.364 D. The dipole moment vector is computed (for either basis) to make an angle of 39° with the C–C single bond axis and points from the methyl carbon toward the hydrogen bonded to the central carbon. This is in agreement with experiment.

Discussion

The bond orbital approach proposed in this paper appears capable of giving a reasonable account of internal rotation in hydrocarbons and at least qualitatively correct results for many molecular properties. Calculations on larger systems such as butane and isobutane are now in progress. Future applications to other molecules containing nitrogen and oxygen are planned.

The method used here is also well suited to calculations on π-electron systems within the framework of π-electron theory. The σ electrons can be placed in orthogonalized bond orbitals and taken into account only through the potential which they exert on the π electrons. Such a method would be much more satisfactory than the older methods since all results for excitation energies, ionization potentials, and other π-electron properties would be computed, *ab initio*, but within a constant σ framework. Calculations along these lines are in progress.

How Efficient Is Diffusion-Controlled Triplet Energy Transfer?[1]

Peter J. Wagner and Irene Kochevar

Contribution from the Chemistry Department, Michigan State University, East Lansing, Michigan 48823. *Received October 7, 1967*

Abstract: The efficiency with which 2,5-dimethyl-2,4-hexadiene ($E_T < 58$ kcal) quenches the triplet-state photoelimination of valerophenone ($E_T > 72$ kcal) has been measured in different solvents. In three tertiary alcohols, $k_q\tau = 160/\eta$ cP M^{-1}. In primary alcohols more viscous than 1-pentanol, $k_q\tau = 125/\eta$ cP M^{-1}. In the less viscous primary alcohols and in alkanes and cycloalkanes, $k_q\tau$ rises as η decreases, but $k_q\tau$ is not a linear function of $1/\eta$. These results suggest that, in solvents where $\eta > 3$ cP, the rate of exothermic triplet-energy transfer from ketones to conjugated dienes is truly limited by and is very nearly equal to the average rate of diffusion in the solution. In less viscous solvents rates of energy transfer are slower than rates of diffusion, indicating that there is enough inefficiency in the energy-transfer process that diffusion apart of triplet ketone and diene molecules can compete with energy transfer during the lifetime of a solution encounter. When the probability that energy transfer will occur during the lifetime of a solution encounter is close to unity, Stern–Volmer quenching plots should curve sharply upward at high quencher concentrations due to nearest neighbor "static" quenching. Quenching of γ-methylvalerophenone by 2,4-hexadien-1-ol in *t*-butyl alcohol displays just such behavior, whereas quenching of γ-phenylbutyrophenone by 1,3-pentadiene in pentane does not. These observations provide evidence that triplet energy transfer is not totally diffusion controlled in solvents of low viscosity.

It is well known that the rate of exothermic triplet energy transfer in solution is influenced by the viscosity of the solvent.[2] It is often assumed[3] that such triplet energy transfer is so efficient that *every* encounter in solution between excited donor and acceptor molecules results in energy transfer, so that the rate of energy transfer is limited by *and equals* the rate of diffusion together of donor and acceptor. Recent reviews[4] provide tables listing the viscosities of common solvents and the rates of diffusion in them as calculated from the Debye equation.[5]

The evidence that energy transfer is diffusion controlled comes from flash spectroscopic studies. In benzene at 25° there is an apparent maximum rate constant for energy transfer of $5 \pm 1 \times 10^9$ M^{-1} sec^{-1} as long as the triplet excitation energy of the donor is 3–4 kcal higher than that of the acceptor (quencher).[6,7] When account is taken of reverse energy transfer from excited quencher back to the original donor, it seems that the energy-transfer process need be no more than 1 kcal exothermic to proceed at the "maximum" rate.[8] That *one* rate constant should describe exothermic energy transfer between literally dozens of donors and acceptors of different structures seems very good intuitive evidence that a common process is rate determining, namely the rate at which excited donor and acceptor molecules can diffuse together in solution.

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(1) Triplet Energy Transfer. III. For a preliminary account, see part II: P. J. Wagner, *J. Am. Chem. Soc.*, 89, 5715 (1967); and P. J. Wagner, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, R118.

(2) G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), A264, 1 (1961).

(3) For example, N. J. Turro, *Chem. Eng. News*, 45, No. 20, 91 (1967).

(4) (a) F. Wilkinson, *Advan. Photochem.*, Vol. 3, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p 248; (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 627.

(5) P. J. W. Debye, *Trans. Electrochem. Soc.*, 82, 265 (1942).

(6) H. J. L. Bäckström and K. Sandros, *Acta Chem. Scand.*, 16, 958 (1962).

(7) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, 88, 4769 (1966).

(8) K. Sandros, *Acta Chem. Scand.*, 18, 2355 (1964).

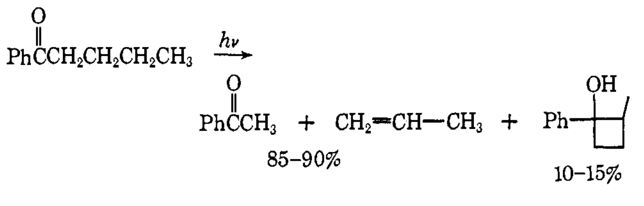
Theory suggests that triplet energy transfer occurs by a very efficient resonance exchange mechanism which requires spatial overlap of the orbitals of donor and acceptor and thus actual collisions of the two molecules.[9] Studies in highly viscous glasses indicate that the rate of the process is inversely proportional to viscosity; consequently, the theoretical model seems sound.[10]

Of more interest to solution photochemists are Osborne and Porter's flash spectroscopic determinations of the rate constants for quenching of triplet naphthalene by 1-iodonaphthalene.[11] They reported that in moderately viscous glycols or paraffin oil–hexane mixtures, quenching rates are inversely proportional to viscosity according to a slightly modified Debye equation which actually is more reasonable theoretically than the standard Debye equation.[12]

$$k_{\text{dif}} = 8RT/2000\eta \qquad (1)$$

Although triplet energy transfer apparently is totally diffusion controlled in very viscous media (in which $k_{\text{dif}} < 10^9\ M^{-1}\ \text{sec}^{-1}$), use of plastics or paraffin oils as solvents is often inconvenient. The "maximum" flash spectroscopic rate constant measured in benzene is only one-third the value predicted by eq 1. Any further "improvements," such as consideration of unequal sizes of donor and acceptor[6] or of possible transient effects,[13,14] serve only to *increase* the predicted value. It is always easy to blame small deviations from theoretical predictions on slight inexactness in the theory; nevertheless, in light of the results obtained in the more viscous media, it seemed a real possibility that rates for triplet energy transfer may be only partially diffusion controlled in the relatively volatile and nonviscous solvents normally used in photochemistry.

This paper describes the results of a systematic study of the dependence of energy-transfer rates on solvent viscosity. The efficiency with which 2,5-dimethyl-2,4-hexadiene quenches the type II photoelimination of valerophenone has been measured in three series of homologous solvents. The ketone's triplet state lies at least 72 kcal above its ground state[15] and is solely responsible for the photoproduction of acetophenone.[16]



$$\text{PhCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{h\nu} \text{PhCOCH}_3 + \text{CH}_2\text{=CH—CH}_3 + \text{Ph—}$$

Since the triplet excitation energy of the diene is below 60 kcal,[17] energy transfer from the ketone triplet to the diene is quite exothermic and normally would be assumed to occur at the diffusion-controlled rate.

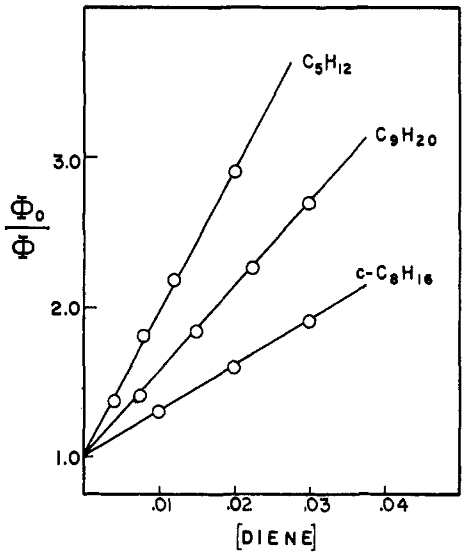


Figure 1. Stern–Volmer plots for quenching of acetophenone formation from valerophenone by 2,5-dimethyl-2,4-hexadiene in three alkanes.

Results

Low-Concentration Quenching. Degassed Pyrex tubes containing solutions 0.10 or 0.20 M in valerophenone, 0.005 M in tetradecane as internal standard, and various concentrations of 2,5-dimethyl-2,4-hexadiene were irradiated in parallel at 3130 Å in a "merry-go-round" apparatus immersed in a water bath held at 25.5°. Since each sample absorbed the same intensity of light, glpc analysis of acetophenone formation provided relative quantum yields directly. Stern–Volmer plots, such as exemplified in Figure 1, were linear, and the values of the slopes obtained in different solvents are listed in Tables I and II as $k_q\tau$ values. Conversions in samples containing no quencher ranged from 5 to 15%. Actinometry with benzophenone–benzhydrol solutions[18] revealed that the quantum yield for disappearance of valerophenone is unity in all the alcohols studied, while Φ_0 for acetophenone formation is 0.90 ± 0.02 in the tertiary alcohols and 0.70 ± 0.02 in all the primary alcohols. The difference can be ascribed to ~20% competing photoreduction in the primary alcohols.[19] In all the alkanes studied as solvents, the quantum yield for disappearance of valerophenone is 0.40 ± 0.02 and the quantum yield Φ_0 for appearance of acetophenone is 0.35 ± 0.02. The fact that Φ_0 is the same for each solvent of a given type is very important because it indicates that there are no spurious quenching impurities which might cause τ values to vary.

Alcohol Solvents. Figure 2 presents plots of $k_q\tau$ values *vs.* reciprocal viscosity for the alcohol solvents studied. The data for the tertiary alcohols can be fitted by the expression $k_q\tau = 160/\eta$ cP M^{-1} and that for the most viscous primary alcohols by $k_q\tau = 125/\eta$ cP M^{-1}. Again, the difference apparently is wholly due to competing photoreduction which shortens τ by ~20%. In the less viscous ($\eta < 3$ cP) primary alcohols, however, the increase in $k_q\tau$ is not as rapid as the increase in $1/\eta$, the value in ethanol being only slightly higher than that in propanol.

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[9] D. L. Dexter, *J. Chem. Phys.*, 21, 836 (1953).

[10] B. Smaller, E. C. Avery, and J. R. Renko, *ibid.*, 43, 922 (1965).

[11] A. D. Osborne and G. Porter, *Proc. Roy. Soc.* (London), A284, 9 (1965).

[12] For a discussion, see H. J. V. Tyrell, "Diffusion and Heat Flow in Liquids," Butterworth and Co., Ltd., London, 1961, p 127.

[13] W. R. Ware and J. S. Novros, *J. Phys. Chem.*, 70, 3247 (1966).

[14] R. M. Noyes, *Progr. Reaction Kinetics*, 1, 129 (1961).

[15] (a) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964); (b) D. R. Kearns and W. A. Case, *ibid.*, 88, 5087 (1966).

[16] P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

[17] R. E. Kellogg and W. T. Simpson, *ibid.*, 87, 4230 (1965).

[18] W. M. Moore and M. Ketchum, *ibid.*, 84, 1368 (1962).

[19] P. J. Wagner, I. Kochevar, and A. Kemppainen, manuscript in preparation.

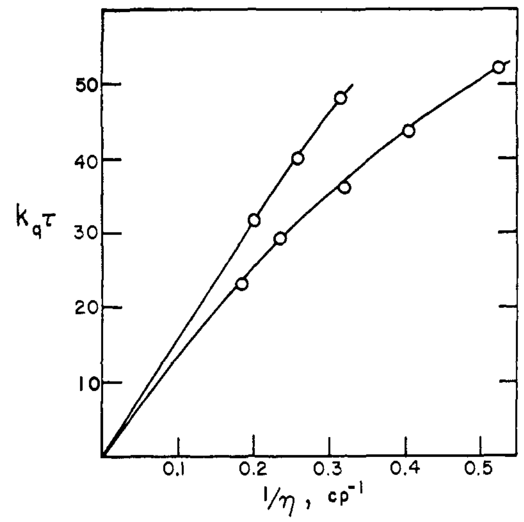

Figure 2. Quenching efficiency of 2,5-dimethyl-2,4-hexadiene toward triplet valerophenone as a function of reciprocal viscosity in alcohol solvents. The top line represents three tertiary alcohols; bottom line, primary alcohols.

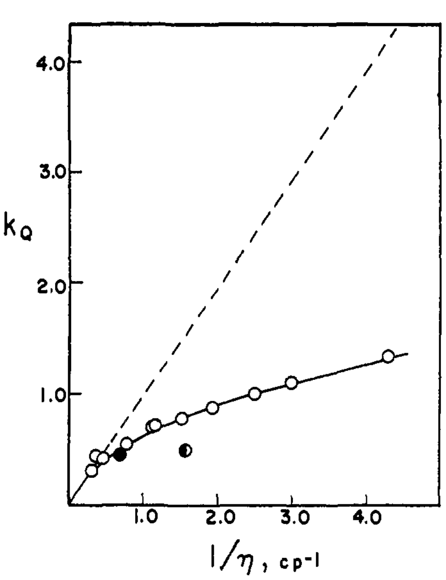

Figure 3. Estimated rate constants for quenching of triplet valerophenone by 2,5-dimethyl-2,4-hexadiene as a function of reciprocal viscosity of alkane solvents. The dotted line is behavior predicted by eq 1; ● is value in hexadecane *vs.* $2/\eta$; ◐ is benzene; k_q is in units of 10^{10} M^{-1} sec^{-1}.

Alkane Solvents. With the assumption that $k_q = 5 \times 10^9$ M^{-1} sec^{-1} in benzene,[6,7] one can calculate $\tau = 7.2 \times 10^{-9}$ sec. It is probably an accurate assumption that this value remains constant in all the hydrocarbon solvents. Not only are the chemical properties of the alkanes very similar, but it has been demonstrated that even major changes in solvent polarity do not greatly change τ.[20] Table II contains values for k_q estimated from the measured quenching constants and an assumed value of 7.2×10^9 sec for τ and values of k_{dif} calculated from eq 1. Figure 3 plots these k_q values *vs.* reciprocal viscosity for the various alkane solvents studied. It is obvious that the relationship, although monotonous, is far from linear. Only in the two most viscous cycloalkane solvents is there any hint of linearity, and the point for hexadecane definitely lies above the curve connecting the cycloalkanes. It has been observed previously that diffusion coefficients in hexadecane are approximately double those predicted by the Stokes-Einstein equation upon which eq 1 is based.[21] The black dot represents the k_q value estimated in hexadecane plotted against $2/\eta$. The dotted line in the figure is that predicted by eq 1. If the value chosen for τ in the alkanes is correct, it would appear that the rate of energy transfer is very close to diffusion controlled only in the most viscous liquid alkanes. It was hoped that the fairly spherical shape of the cycloalkane molecules would preclude serious deviations from theoretical behavior such as found for the long, rod-like hexadecane molecules. The agreement between k_q and k_{dif} in cyclooctane and in the 7:5 mixture of cyclododecane:cyclooctane is some measure of the validity of this hope.

Table I. Efficiency with Which 2,5-Dimethyl-2,4-hexadiene Quenches Photoelimination of Valerophenone in Alcohol Solvents

Solvent	η, cP[a]	$k_q\tau_0$, M^{-1} [b]
t-Amyl alcohol	3.16	48
t-Butyl alcohol	3.88	40
Triethylcarbinol	5.02	31.5
Ethanol	1.07	61
1-Propanol	1.91	52
1-Butanol	2.48	43.5
1-Pentanol	3.13	36
1-Hexanol	4.30	30
1-Heptanol	5.46	23

[a] Viscosity of solution containing 0.2 *M* valerophenone, at 25.5°. [b] Generally the average of duplicate measurements.

Table II. Efficiency with Which 2,5-Dimethyl-2,4-hexadiene Quenches Photoelimination of Valerophenone in Alkane Solvents

Solvent	η, cP[a]	$k_q\tau_0$,[b] M^{-1}	k_q,[c] 10^{10} M^{-1} sec^{-1}	k_{dif},[d] 10^{10} M^{-1} sec^{-1}	α
Benzene	0.634	36	0.50	1.55	0.32
Pentane	0.233	95	1.32	4.20	0.31
Hexane	0.334	79	1.10	2.93	0.375
Heptane	0.400	72	1.00	2.45	0.41
Octane	0.519	63	0.88	1.90	0.46
Nonane	0.660	56	0.78	1.49	0.525
Decane	0.846	51	0.71	1.16	0.61
Cyclohexane	0.884	48	0.67	1.11	0.60
Cycloheptane	1.30	39	0.54	0.75	0.72
Cyclooctane	2.16	30.5	0.42	0.45	0.93
Cyclododecane-cyclooctane[e]	3.15	21.5	0.30	0.31	0.97
Hexadecane	2.85	32.5	0.45	...	...

[a] Measured at 25.5° on solutions 0.2 *M* in valerophenone. [b] Average of duplicate measurements, generally reproducible to ±2%. [c] Values all based on assumed value in benzene, see text. [d] Values predicted by eq 1. [e] A 7:5 w/w mixture.

High-Concentration Quenching. Degassed *t*-butyl alcohol solutions of γ-methylvalerophenone with 2,4-hexadien-1-ol as quencher were irradiated at 3660 Å and analyzed as usual. The Stern-Volmer plot obtained at low concentrations of the dienol is displayed in Figure 4. It is perfectly linear with a slope, equal to $k_q\tau$, of 7.6 M^{-1}. Relative quantum yields of acetophenone formation were also measured at fairly high dienol concentrations, and the results shown in Figure 5 demon-

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(20) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5898 (1967).

(21) J. H. Gorrell, Jr., and J. T. Dubois, *Trans. Faraday Soc.*, **63**, 347 (1967).

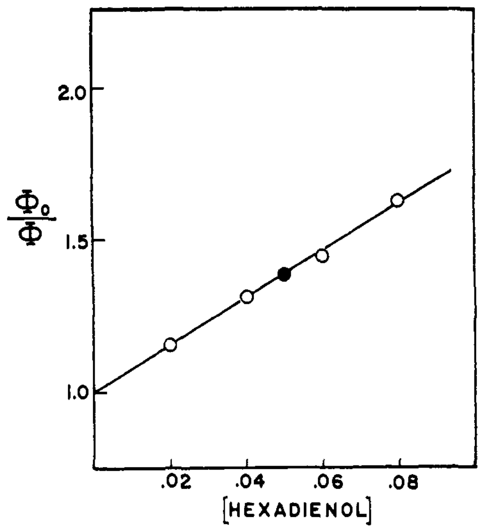

Figure 4. Quenching of acetophenone formation from γ-methylvalerophenone in *t*-butyl alcohol by low concentrations of 2,4-hexadien-1-ol. The solid circle was obtained in a separate experiment.

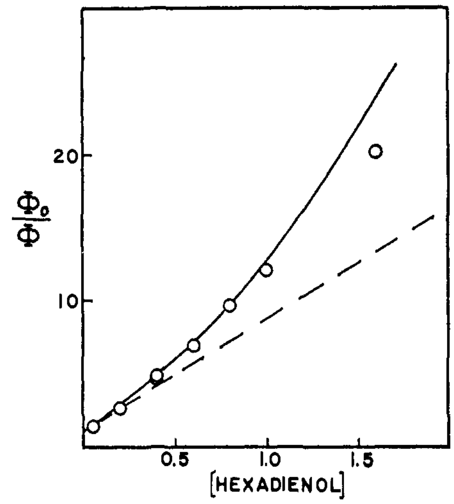

Figure 5. Quenching of acetophenone formation from γ-methyl valerophenone by high concentrations of 2,4-hexadien-1-ol in *t*-butyl alcohol. The dashed line is extrapolation of low concentration data; solid curve indicates behavior expected for static quenching.

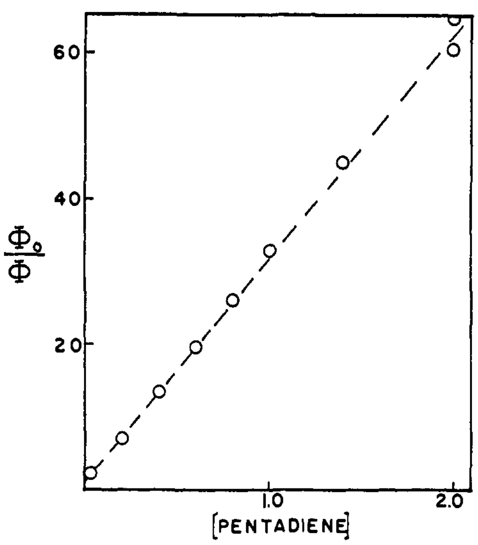

Figure 6. Quenching of acetophenone formation from γ-phenylbutyrophenone by moderate concentrations of *cis*-1,3-pentadiene in pentane. The dashed line is extrapolation of low-concentration data.

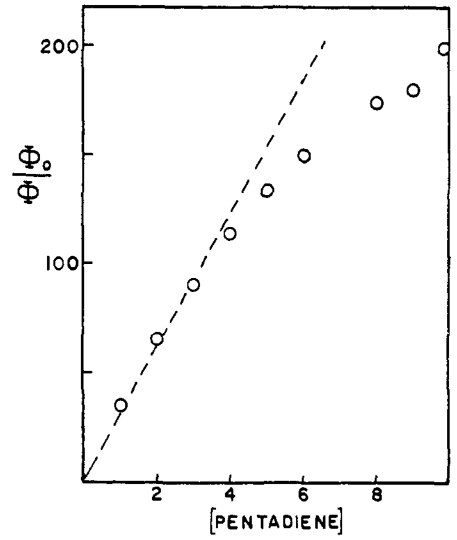

Figure 7. Quenching of acetophenone formation for γ-phenylbutyrophenone by high concentrations of *cis*-1,3-pentadiene in pentane. The dashed line is extrapolation of low-concentration data.

strate a marked divergence from normal Stern–Volmer kinetics.

A similar high-concentration quenching study was performed on the type II cleavage of γ-phenylbutyrophenone in pentane with 1,3-pentadiene as quencher. Figures 6 and 7 depict Stern–Volmer plots of the results at moderate and at high diene concentrations. The low-concentration slope of 30.5 M^{-1} is represented by the dotted line in both figures, and it is apparent that there is little deviation at moderate quencher concentrations. Above 1 *M* diene, the plot starts to curve upward, then curves back down to a value of 200 in neat diene.

Discussion

Diffusion Theory. von Smoluchowski's solution[22] of Fick's equations, as Svenshnikoff[23] applied it to fluorescence quenching, yields the following expression for the rate at which two reacting species D and A diffuse together, where σ is the sum of the collision radii of D and A, $\mathfrak{D}$ is the sum of their diffusion coefficients, *N* is Avogadro's number, and τ is the lifetime of the excited donor D.

$$k_{\text{dif}} = \frac{4\pi\sigma\mathfrak{D}N}{1000}\left[1 + \frac{\sigma}{\sqrt{\mathfrak{D}\tau}}\right] \tag{2}$$

If the Stokes–Einstein equation is used to relate diffusion coefficients to viscosity, the following equation results.[11,12]

$$k_{\text{dif}} = \frac{8RT}{2000\eta}\left[1 + \frac{\sigma}{\sqrt{\mathfrak{D}\tau}}\right] \tag{3}$$

Equation 3 is nothing more than eq 1 with the added "transient" factor in brackets. In flash spectroscopic determinations of triplet quenching rates, where $\tau >$

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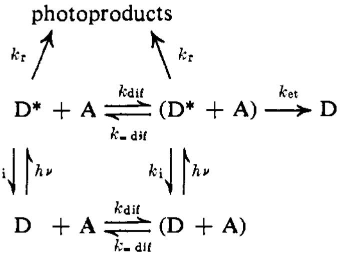
[22] M. von Smoluchowski, *Z. Physik. Chem.*, **92**, 129 (1917).

[23] B. Svenshnikoff, *Acta Physiochim. USSR*, 3, 257 (1935); 4, 462 (1936).

10^{-6} sec, transient terms are negligible. Their effect on steady-state quenching studies should be to cause an upward curve in Stern–Volmer plots, provided that $\tau_0 < 10^{-7}$ sec, where τ_0 is the lifetime of the triplet donor in the absence of any added quencher. This curvature should become apparent even at rather low concentrations of quencher if the values of $\mathfrak{D}$ and particularly of τ_0 are low enough, since $\tau = (1/\tau_0 + k_q[A])^{-1}$.

Several authors have pointed out that one of the boundary conditions chosen by von Smoluchowski cannot be generally correct,[13,14,24] and they have advanced rather complex modifications of eq 2 wherein σ in effect is corrected for any inefficiency in the reaction between D and A. This correction lowers the value of both the transient and nontransient terms in eq 2 and 3. Since the transient term contains σ^2, its importance declines rapidly as the efficiency of reaction between D and A falls below unity.

A phenomenon which generally has been ignored in studies of triplet energy transfer is "static" quenching. If, in our case, a ketone molecule were to absorb a photon while a diene molecule was a nearest neighbor in solution, that particular excited ketone molecule would immediately be quenched, if energy transfer to the diene were 100% efficient, and could not enter into the normal competition between chemical reaction and diffusional quenching. This phenomenon was postulated years ago for fluorescence quenching by Bowen and Metcalf[25] and has been elaborated more recently by Weller.[26] If a sizable percentage of excited molecules are formed with quencher molecules as nearest neighbors, both diffusional and static quenching will occur competitively. The following scheme represents the various reactions of interest. The rate constants k_r and k_i describe chemical reaction and radiationless decay of the excited state, respectively, and are assumed to be unaffected by the presence of a quencher molecule A as nearest neighbor. A rate for radiative decay could be included, but its value would be much smaller than any other considered in this paper.



From the above scheme the following expression can be derived[26] for relative quantum yields of product formation as a function of quencher concentration, where α is the probability that energy transfer will occur during the lifetime of a solution encounter and u equals the fraction of light absorbed by (D + A) complexes.

$$\phi_0/\phi = \frac{1 + k_q[A]\tau_0}{1 - \alpha u} \tag{4}$$

$$1/\tau_0 = k_r + k_i \tag{5}$$

$$k_q = \alpha k_{dif} \tag{6}$$

$$\alpha = k_{et}/(k_{et} + 1/\tau_0 + k_{-dif}) \tag{7}$$

If one assumes a purely statistical distribution of molecules in solution, one can estimate values for u as a function of n, the average number of nearest neighbor molecules in solution, and of x_A, the mole fraction of quencher molecules.[27]

$$u = 1 - (1 - x_A)^n \tag{8}$$

There are two limiting cases in which eq 4 collapses into the normal Stern–Volmer expression: (1) whenever α is very small, and (2) whenever the concentration of quencher is so low that $\mu \sim 0$. The upward curvature predicted by eq 4 for Stern–Volmer plots can occur only when α is close to unity and then only at sufficiently high concentrations of quencher that a significant fraction of donor molecules have at least one quencher molecule as nearest neighbor at the moment of excitation.

$$\phi_0/\phi = 1 + k_q[A]\tau_0 \tag{9}$$

An interesting effect of static quenching arises when a quencher is used as solvent, so that $u \sim 1$. When every D* molecule is always in contact with quencher molecules, there is no diffusional quenching. The only product formation from D* must come from direct competition between k_r and k_{et}, so that eq 4 becomes eq 10, which provides a lower limit for the value of k_{et}.

$$\phi_0/\phi = 1 + k_{et}\tau_0 \tag{10}$$

Efficiency of Triplet Energy Transfer. The results presented here indicate that in the case of exothermic triplet energy transfer from an excited ketone to a conjugated diene, quenching rates definitely are not inversely proportional to viscosity in solvents where $\eta < 3$ cP. Since triplet butyrophenone is quenched with equal efficiency by several different quenchers,[28] it must be concluded that the present results are general and are not restricted to dienes as quenchers. The results obtained in the fairly viscous alcohols and cycloalkanes, where k_q values are very nearly inversely proportional to viscosity and where it therefore is valid to conclude that k_q very nearly equals k_{dif}, can be considered as extensions of Osborne and Porter's studies[11] into less viscous media. Although Osborne and Porter found that eq 1 predicts triplet quenching rates in both glycol and paraffin solvents, other studies[13] suggest that eq 1 underestimates k_{dif} by about half for alcohol solvents. However, if diffusion coefficients in alcohols were double those predicted by the Stokes–Einstein equation upon which eq 1 is based, considerably more curvature would be expected in Figure 3, analogous to that in Figure 4 for η values from 2 to 1 cP.

Since k_q values are not proportional to $1/\eta$ in low-viscosity solvents, two possibilities present themselves as reasons: either $k_q < k_{dif}$ or $k_q = k_{dif}$, but eq 1 fails to predict correct values of k_{dif} in low viscosity solvents.

The latter possibility does not seem very likely. The smaller the solvent molecules, the more nearly ideal their behavior ought to be. Moreover, rate

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(24) F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, 4, 425 (1949); F. C. Collins, *ibid.*, 5, 499 (1950).

(25) E. J. Bowen and W. S. Metcalf, *Proc. Roy. Soc.* (London), **A206**, 437 (1951).

(26) A. Weller, *Z. Physik. Chem.* (Frankfurt), 13, 335 (1957); *Discussions Faraday Soc.*, 27, 28 (1959); *Progr. Reaction Kinetics*, 1, 189 (1961).

(27) H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1911 (1964).

(28) P. J. Wagner, *ibid.*, **89**, 2820 (1967).

constants with values very close to those predicted by eq 1 have been measured in hexane[29] and in heptane[13] for fluorescence quenching, so that rates of diffusion must exceed those measured here for k_q.

If, then, $k_q < k_{dif}$ in low-viscosity solvents, the efficiency of triplet energy transfer must be considerably lower than is normally assumed. The process must be slow enough that, once excited ketone and ground-state diene molecules have diffused together, their diffusion apart can compete with actual energy transfer. This conclusion might have been predicted, since Rebbert and Ausloos have reported that in the gas phase some 50 collisions are required for conjugated dienes to quench triplet acetone.[30] Simple calculations[31] predict just about that number of effective collisions during the lifetime of a prolonged solution encounter in solvents of very low viscosity.

The contrast between the high concentration quenching results in *t*-butyl alcohol and in pentane support the conclusion that quenching is less than 100% diffusion controlled in the latter solvent. As the previous discussion indicated, consideration either of possible transient effects or of static quenching suggests that Stern–Volmer plots should curve upward only if α is close to unity. Figures 5 and 6 depict quenching of ketones with very similar triplet lifetimes over the same range of diene concentrations in the two solvents. Little deviation from linearity is evident in pentane in contrast to the marked upward curvature in *t*-butyl alcohol.

The solid curve in Figure 5 is that predicted by eq 4 with $\alpha = 1$, and by eq 8 with $n = 4$. Since values of n are difficult to guess accurately, the "theoretical" curve is intended merely to indicate what kind of departure from normal Stern–Volmer kinetics might be produced by static quenching. There is some doubt whether transient effects contribute much to the curvature. If a reasonable value[13] of 6 Å is chosen for σ, and if measured estimates for $\mathfrak{D}$ and τ_0 are plugged into eq 3, much more curvature would be predicted for Figure 5 and decided curvature should be evident in Figure 4 if transient terms are important.

The practical implications of the conclusion that $k_q < k_{dif}$ in nonviscous solvents are, at first glance, somewhat grim. At the moment, quenching studies of the Stern–Volmer type are the only way of ascertaining the reactivity of excited ketones, since the short excited-state lifetimes of most reactive ketones prevent their decay kinetics from being measured directly by current flash spectroscopic equipment. However, such studies can provide accurate knowledge of the reactivities of excited states only if accurate values for quenching rate constants are known.

Fortunately, the data in Table II can be treated so as to allow prediction of k_q values. The efficiency of energy transfer, α, is determined primarily by the competition between k_{et}, the rate at which energy is transferred once donor and acceptor have diffused together, and k_{-dif}, the rate at which the two species diffuse apart.[32] Normally and in the reaction studied in this work, $1/\tau_0$ is so much smaller than k_{-dif} that its contribution to the lifetime of a solution encounter can be ignored.

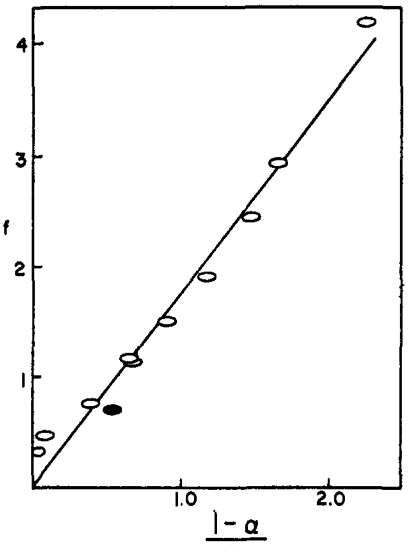

Figure 8. Plot of k_{dif} *vs.* $(1 - \alpha)/\alpha$. The slope is proportional to k_{et} according to eq 13. k_{dif} is in units of 10^{10} M^{-1} sec^{-1}.

As Table II indicates, α begins falling appreciably below unity as η becomes lower than 3 cP. The value of k_{et} presumably remains constant throughout, since the same donor–acceptor pair is involved in the various different solvents. The problem is to decide on reasonable values for k_{-dif}, which must be directly proportional to k_{dif}.

$$k_{-dif} = \xi k_{dif} \tag{11}$$

$$\alpha = k_{et}/(k_{et} + \xi k_{dif}) \tag{12}$$

$$k_{dif} = k_{et}(1 - \alpha)/\alpha\xi \tag{13}$$

In Figure 8 the data in Table II are plotted according to eq 13. The slope of the line is k_{et}/ξ and equals $1.8 + 0.1 \times 10^{10}$ sec^{-1}. Empirically, one could assume any constant value for ξ in order to estimate α for a nonviscous solvent as a function of viscosity. Some indication of the actual magnitude of ξ can be extracted from the quantum yield of acetophenone formation obtained upon irradiation of γ-phenylbutyrophenone in neat *cis*-1,3-pentadiene. Since this quantum yield may contain a trace of singlet reaction,[33] the ***minimum*** value of $k_{et}\tau_0$ is 200. Low-concentration quenching results yielded a value of 30.5 M^{-1} for $k_q\tau_0$. Since from Table II, k_q in pentane (which has almost the same viscosity as pentadiene) is 1.3×10^{10} M^{-1} sec^{-1}, τ_0 can be estimated as 2.3×10^{-9} sec. Therefore $k_{et} \geq 9 \times 10^{10}$ sec^{-1}, and $\xi \sim 5$.

Random-walk theory predicts the following value for the lifetime of a solution encounter.

$$1/k_{-dif} = \sigma^2/6\mathfrak{D} \tag{14}$$

Equations 2 and 14 together yield the following more explicit form of (11).

$$k_{-dif} = \frac{3000k_{dif}}{2\pi N\sigma^3} \tag{15}$$

With the assumption that $\sigma = 6$ Å,[13] eq 15 yields a value

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(29) J. T. Dubois and R. L. van Hemert, *J. Chem. Phys.*, 40, 923 (1964).

(30) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, 87, 5569 (1965).

(31) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 496.

(32) R. F. Borkman and D. R. Kearns, *J. Am. Chem. Soc.*, 88, 3467 (1966), have worked out a similar scheme. They do not, however, consider the case in which k_{et} and k_{-dif} are competitive.

(33) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

of 4 for ξ. The agreement between this crude theoretical value and the empirical value of 5 seems more than satisfactory.

It should be noted that the $k_q\tau_0$ value obtained in benzene does not lie on the same curve in Figure 3 as those obtained in alkanes. Consequently, the point for benzene lies far off the line described by the alkane solvent points in Figure 8. The reason for this discrepancy is not known and is under investigation. The points for the two most viscous cycloalkane solvents obviously lie above the line determined by the other points in Figure 8. This discrepancy may indicate that the value chosen for τ_0 is slightly low or that ξ is not constant in all the solvents studied.

The theoretical implications of the conclusion that $k_q < k_{dif}$ even in the case of exothermic triplet energy transfer are very interesting. The overlap of orbitals required to produce triplet energy transfer might demand a preferred relative configuration of donor and acceptor molecules, and El-Sayed has in fact provided an experimental demonstration of such a requirement.[34] If configurational effects are large enough to lower k_{et} two orders of magnitude below the collision frequency, rate constants for exothermic energy transfer ought to show some variance. Obviously, much further work is needed to discover the magnitude of steric effects in triplet energy transfer and to explain why so many different donors and acceptors seem to undergo energy transfer at such similar rates in benzene.[6-8] Actually, measured flash spectroscopic rate constants for quenching do vary by as much as 50%, but the values are all within experimental error of one another. It is quite possible that the experimental error has hidden real but small differences. As long as α is even close to unity, rather large changes in k_{et} produce only small changes in k_q.

Experimental Section

All hydrocarbon solvents were commercial reagent grade materials which were washed with sulfuric acid until no further coloration of the acid layer took place. They were then treated with aqueous base and dried over calcium chloride. The more volatile ones were then distilled from phosphorus pentoxide, while the high-boiling ones were passed through a column of activated alumina. Alcohol solvents were reagent grade distilled from sodium.

Aldrich valerophenone was distilled under reduced pressure and then recrystallized from pentane. Aldrich 2,5-dimethyl-2,4-hexadiene was recrystallized from itself. Aldrich 2,4-hexadienol was recrystallized ten times from pentane until its optical density at 3660 Å was only 0.40. The impurity was assumed to be the corresponding aldehyde. Chemical Samples Co. *cis*-1,3-pentadiene was used as received. The γ-methylvalerophenone was prepared by addition of phenylmagnesium bromide to 4-methylvaleronitrile. Aldrich γ-phenylbutyrophenone was recrystallized several times from pentane.

Viscosities of the actual reaction solutions were determined with a standard Ostwald viscosimeter at 25.5°. Addition of the hexadienol to *t*-butyl alcohol produces only a negligible change in viscosity; the same behavior obtains for the pentadiene–pentane system.

Low-concentration quenching studies were performed as described previously.[28] The high-concentration studies were done by irradiating the samples much longer than usual. Sample tubes containing no quencher were irradiated for short periods at the beginning, middle, and end of each long run; the average amount of reaction in them was assumed to be proportional to Φ_0. The data used to plot Figure 5 were corrected for up to 10% absorption by the dienol at the highest concentration. The data for quenching of γ-phenylbutyrophenone had to be corrected for formation of styrene, which itself is a very efficient quencher.

All irradiations were performed on samples contained in degassed, sealed 13-mm o.d. Pyrex culture tubes. These were held in the turntable of a "merry-go-round" apparatus, at the center of which was a 450-W Hanovia medium-pressure mercury arc. The 3130-Å line was isolated by a filter solution containing 0.002 *M* potassium chromate in 1% aqueous potassium carbonate. The 3660-Å line was isolated with a set of Corning No. 7-83 filters.

Analyses were performed both on Aerograph Model 600 Hy-Fi gas chromatographs and later on a Model 1200 Hy-Fi. A 10 ft × 1/8 in. column containing 4% QF-1 and 1% Carbowax 20M on 60–80 AW, DMSC treated Chromosorb G was used to analyze for acetophenone formation. On-column injection was very useful in preventing the higher boiling solvent peaks from tailing too much.

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[34] J. K. Roy and M. A. El-Sayed, *J. Chem. Phys.*, 40, 3442 (1964).