mixture in isopropyl alcohol resulted in a precipitation of sodium chloride and a marked increase in the second-order rate constant. A similar increase in rate constant was observed for the reaction of benzophenone with lithium borohydride.

Addition of sodium iodide (soluble in isopropyl alcohol) to the reaction mixture of sodium borohydride and acetone in isopropyl alcohol did not influence the rate significantly. This indicates that the reaction is not very sensitive to general salt effects. However, the addition of lithium iodide results in an increase in rate which rises linearly with the amount of lithium iodide.

It therefore appears that in aqueous solution there is no difference in the rate of reaction of lithium or sodium borohydride with acetone, whereas in isopropyl alcohol there is a major difference in rates. These results suggest that in water the reaction of borohydride with acetone involves the dissociated ion, and the positive ion present does not influence the rate of reaction. In a solvent such as isopropyl alcohol the alkali metal borohydride must be largely present as undissociated ion-pairs. Consequently, the reactivity of the ion-pair would be expected to depend somewhat on the precise cation present in the reaction mixture.

The reactivity of lithium borohydride in isopropyl alcohol is increased by dissolved lithium chloride. Similarly, the presence of lithium iodide increases the reactivity of sodium borohydride somewhat. The increase with the smaller concentrations of lithium iodide is moderate, suggesting that the exchange to form lithium borohydride in solution cannot be complete—we are evidently dealing with an equilibrium system of sodium and lithium borohydrides.

The data do not permit a definite explanation of the effect of excess lithium chloride or iodide on the rate. Conceivably, the excess salt modifies the nature of the ionic clusters in the solvent, or conceivably the lithium ion may serve two functions. On the one hand, it may serve to activate the borohydride ion in the ion-pair (or ionic cluster) through its polarizing influence. On the other, it may also serve to activate the carbonyl group of the ketone through its known ability to coördinate with such groups.

Experimental Part

An Experimental Study of Energy Transfer between Unlike Molecules in Solution

BY WILLIAM R. WARE

The transfer or excitation between polynuclear aromatic hydrocarbons has been studied using fluorescence lifetime measurements. Second order rate constants three to twelve times greater than predicted by diffusion theory have been observed, and correlation has been obtained between the experimental results and the theory of weak resonance interaction.

Introduction

While the subject of energy transfer between unlike molecules in solution through a resonance interaction has received considerable theoretical attention,[1-3] there have been relatively few critical

(1) Th. Förster, "Fluoreszenz Organisher Verbindungen," Vandenhoeck and Ruprecht, Göttingen, 1951.

(2) Th. Förster in "Comparative Effects of Radiation," ed. by M. Burton, J. S. Kirby-Smith and J. L. Magee, John Wiley and Sons, Inc., New York, N. Y., 1960.

(3) Th. Förster, *Discussions Faraday Soc.*, 27 (1959).

experiments reported.[3,4] One of the contributing factors to this situation is the difficulty of unambiguously interpreting fluorescence intensity measurements. This arises from the following circumstances: (a) conditions for resonance transfer favor the trivial process of fluorescence absorption; (b) the acceptor frequently exhibits some absorption in the region where the sensitizer ab-

(4) E. J. Bowen and Robert Livingston, *J. Am. Chem. Soc.*, **76**, 6300 (1954).

sorbs strongly; (c) both sensitizer and acceptor absorb their own radiation to an appreciable extent.

Since these problems are for the most part avoided when fluorescence lifetime measurements are used to examine the kinetics of such processes, it appeared desirable to examine several systems in order to make a quantitative study of this phenomenon.

Fluorescence lifetime measurements were made using the phase shift technique developed by Bailey and Rollefson and others.[5,6] This technique makes use of the fact that if fluorescence is excited by sinusoidally modulated light, the emission will be sinusoidally modulated but with a shift in phase which may in general be related to the lifetime of the species involved. If we are dealing with the mechanism

$$A \xrightarrow{h\nu} A^* \qquad\qquad v_1 = a + b \sin \omega t \qquad (1)$$
$$A^* \rightarrow A + h\nu_f \qquad\quad v_2 = k_2[A^*] \qquad\qquad (2)$$
$$A^* \rightarrow A \text{ (or } A^* \rightarrow A' \rightarrow A) \quad v_3 = k_3[A^*] \qquad\qquad (3)$$
$$A^* + A \rightarrow 2A \qquad\qquad v_4 = k_4[A][A^*] \qquad (4)$$
$$A^* + B \rightarrow A + B^* \qquad v_5 = k_5[A^*][B] \qquad (5)$$
$$B^* \rightarrow B + h\nu_f \qquad\quad v_6 = k_6[B^*] \qquad\qquad (6)$$
$$B^* \rightarrow B \text{ (or } B^* \rightarrow B' \rightarrow B) \quad v_7 = k_7[B^*] \qquad\qquad (7)$$
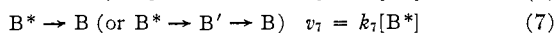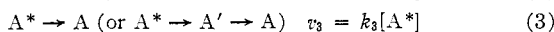
the phase shift ϕ is easily shown[5] to be

$$\tan \phi = 2\pi f \tau_A \qquad\qquad (8)$$

where f is the light modulation frequency and

$$1/\tau_A = k_2 + k_3 + k_4[A] + k_5[B] \qquad (9)$$

It is assumed that only the fluorescence of A is involved in the measurement and that only the fundamental frequency f is used. This is accomplished with light filters and tuned circuits. One of the most useful aspects of the method is the possibility of a linear relationship between $1/\tau$ and [B], the concentration of the acceptor or quencher, giving k_5 from the slope. The sensitizer–acceptor pairs investigated were: (a) anthracene–perylene; (b) anthracene–rubrene; (c) 9,10-dichloroanthracene–perylene; (d) 9,10-dichloroanthracene–rubrene; (e) perylene–rubrene. Originally it was planned to include 1-chloroanthracene as a sensitizer in order to compare results with the experiments of Bowen and Livingston,[4] but the lifetime of 1-chloroanthracene was too short and the fluorescence efficiency too low to permit accurate quenching measurements.

Experimental

The equipment used to determine fluorescent lifetimes was similar in many respects to that described by Bailey and Rollefson.[5] A block diagram is given in Fig. 1. Light from a General Electric H85 d.c. operated mercury lamp was passed through a Bausch and Lomb prism monochromator, then through the light modulating water tank and finally through the reference cell containing a BaSO₄ sol and the cell containing either a sol or the fluorescent solution. The two light beams thus generated were detected by 1P21 photomultipliers and coupled to the phase shift circuits by cathode followers. The phase shift circuits were identical with those of Bailey and Rollefson and had their outputs connected to a balanced antenna coil of a crystal controlled converter. This converter provided an output of 470 Kc. which was
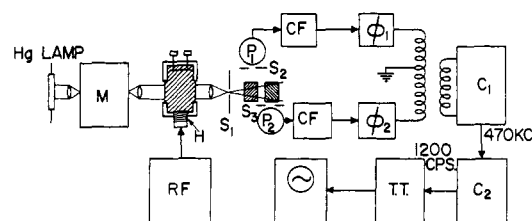

Fig. 1.—Block diagram of phase shift apparatus: M, monochromator; S_1, S_2, S_3, adjustable slits; P_1, P_2, photomultipliers; CF, cathode follower; ϕ_1, ϕ_2, phase shift circuits; C_1, crystal controlled converter; C_2, Hammarlund HC-10 converter; T.T., Twin-T amplifier; RF, r. f. generator; H, transducer holder.

amplified by a Hammarlund HC-10 converter. The output consisted of a 1200 c.p.s. signal generated by the beat frequency oscillator of the HC-10. This was amplified in a narrow band twin-T amplifier and displayed on the y axis of an oscilloscope. The horizontal sweep was driven at 60 c.p.s.

The ultrasonic modulator utilized a crystal controlled oscillator driving a push–pull r.f. amplifier which was coupled to an x-cut quartz transducer using a circuit similar to that described by Venetta.[7] The modulator unit consisted of a water tank 3″ × 4″ × 5″ with a cylindrical transducer holder mounted in one end. The direction of propagation was perpendicular to the light beam and in the horizontal plane. Both the transducer holder and a reflector at the opposite end of the tank were adjustable to achieve an optimum standing wave. Slit S_1 was adjustable for both horizontal movement and width, while slits S_2 and S_3 were adjustable for width and were used to change the signal amplitude. The equipment was designed to operate at 5.200 M.c. and 10.60 M.c. (i.e., with the transducer driven at either 2.6 or 5.3 M.c.).

The precision variable air capacitor used to shift phase was calibrated in the phase shift circuit using a Wayne–Kerr Universal Bridge (B221) and was accurate to 0.1 $\mu\mu$F. The tube parameters μ and r_p of the 6J6 tubes were determined directly by the method of static increments[8] at the operating point found to be appropriate by measurements in a dummy phase shift circuit. Interelectrode capacity was determined with the Wayne–Kerr bridge.

Measurements were carried out as described by Bailey and Rollefson. Two types of cells were used. For very dilute solutions and all sols, a cell having a 1 cm. square cross section was convenient. For more concentrated solutions, a flat cell 1 mm. thick was employed and was oriented at 45° to the incident beam permitting the photomultiplier to view the illuminated face. All cells were designed to permit the removal of oxygen with purified helium prior to the measurements. Corning and Wratten filters were employed behind slits S_2 and S_3 to isolate the sensitizer fluorescence from both the scattered or reflected incident light and acceptor fluorescence and to avoid interference from fluorescence scattered by the reference sol. Care was taken to avoid interference from filter fluorescence. The 365 mμ mercury line was used to excite anthracene and 9,10-dichloroanthracene and the 405 mμ line was used for perylene.

Absorption spectra were run on a Beckman DU spectrophotometer. Fluorescence spectra were determined with the aid of the fluorescence spectral attachment for the DU. However, a 931-A photomultiplier was used at the exit slit of the monochromator and the measurement of photocurrent made with an accurate sensitive vacuum tube voltmeter. The fluorescence spectral apparatus was calibrated with quinine bisulfate,[9] and all spectra were taken on solutions dilute enough to render self-absorption negligible.

Anthracene was obtained from Harshaw Chemical Company and was a special scintillation grade which had not been subjected to the crystal growing process. It was recrystallized from benzene or toluene. Perylene was obtained from Terra Chemical Company and was purified by silica gel chromatography of its recrystallized picrate. A pure

(5) E. A. Bailey and G. K. Rollefson, J. Chem. Phys., **21**, 1315 (1953).

(6) A. M. Bonch-Brevich, et al., Izvest. akad. nauk, Ser. fiz, **20**, 591 (1956).

(7) B. D. Venetta, Rev. Sci. Inst., **30**, 450 (1959).

(8) F. E. Terman and S. M. Pettit. "Electronic Measurements," McGraw-Hill Book Co., New York, N. Y., 1952, pp. 296–297.

(9) W. H. Melhuish, J. Phys. Chem., **64**, 762 (1960).

sample of 9,10-dichloroanthracene was obtained from J. C. Ware. It had been prepared from pure anthracene. Rubrene, in a sufficiently pure state as indicated by C–H analysis and spectral evidence, was obtained from Aldrich Chemical Company. Dry thiophene-free reagent benzene was used for all the experiments.

Sensitizer Lifetimes.—The sensitizer lifetimes given in Table I refer to dilute solutions where fluorescence absorption

TABLE I

SENSITIZER LIFETIMES

Substance	τ (sec.) $\times 10^9$
Anthracene	4.1 ± 0.1
Perylene	$5.2 \pm .1$
Rubrene	$15.4 \pm .4$
9,10-Dichloroanthracene	$9.6 \pm .2$

and re-emission do not introduce an error resulting from an apparent increase in lifetime. Of the various sensitizers used, only anthracene showed ideal behavior in that its lifetime, as measured in a 1 mm. flat cell viewed at 45°, remained constant as the concentration was increased until self-quenching set in. The self-quenching curve ($1/\tau_s$ vs. [A]) was linear and extrapolated to the dilute solution value of $1/\tau_s$. The quenching constant k_4 was found to be $7.4 \times 10^9 M^{-1}$ sec.$^{-1}$ which compared favorably with the value of 7.3×10^9 calculated from Bowen's Stern–Volmer constant.[10] The value for the lifetime of anthracene is in reasonably good agreement with that reported by Metcalf[11] and by Knau.[12] The value of 1.60×10^{-8} sec. obtained for acridone (saturated aqueous solution) is in agreement with the value obtained by Bailey and Rollefson[5] but not with Metcalf's of 1.49×10^{-8} sec. It is considered likely that the lack of agreement between various investigators is due in part to the calibration of the phase shift circuit and in particular the vacuum tube.

Measurements of k_4 over a temperature range of 10–55° gave a linear plot of k_4 vs. T/η with an intercept ($T/\eta = 0$) of $2.4 \times 10^9 M^{-1}$ sec.$^{-1}$. The slope gave $P = 0.42$, assuming

$$k_4 = \frac{8PRT}{3 \times 10^3 \eta} + k_4' \qquad (10)$$

where η is the viscosity and P the probability factor, which would give a collisional constant of $4.95 \times 10^9 M^{-1}$ sec.$^{-1}$ and a temperature–viscosity independent constant of 2.5×10^9.

Perylene and 9,10-dichloroanthracene both had high enough fluorescence efficiencies and absorbed enough of their own fluorescence to make self-quenching studies inaccurate, but these presented no problem since reasonably dilute solutions could be used for energy transfer studies.

Energy Transfer Measurements.—Table II lists the second order rate constants obtained from plots of $(1/\tau_s)$ vs. [B] for various sensitizer–acceptor pairs. These plots were linear and extrapolated to the value of $1/\tau_s$ for [B] = 0. The concentration ranges used were dictated by the following considerations: (a) accurate lifetime measurements could not be made below 1.6×10^{-9} sec. due to the small phase angle change; (b) large concentrations of acceptor also decreased the sensitizer fluorescence intensity to the point where the inadequate signal strength was obtained and accurate measurements were impossible. The range over which the acceptor concentration could be varied was thus limited to very dilute solutions, and Stern–Volmer behavior could be expected in spite of the inverse sixth power dependence of resonance interaction on distance.[3] It is estimated that the uncertainty in the measured second order rate constants is about 15%.

The rate constants for transfer and the sensitizer lifetimes did not change when the modulation frequency was changed from 5.2 to 10.6 Mc, indicating that the eq. 8 is obeyed and the assumptions implicit in eqs. 1 to 7 are reasonably valid. Unfortunately, it was not practical to use a large number of frequencies, because of the requirements of crystal frequency control, the large number of tuned circuits involved and the frequency tolerance required in the transducer.

(10) E. J. Bowen, *Trans. Faraday Soc.*, **50**, 97 (1954).

(11) W. S. Metcalf, *J. Chem. Soc.*, **3729** (1960).

(12) V. H. Knau, *Z. Naturforsch.*, **12A**, 881 (1957).

These results were compared with the theory elaborated by Förster[1,2] for a weak interaction involving allowed dipole transitions in which the "critical distance" R_0 for equal probability of transfer and deactivation by other processes is given by

$$R_0^6 = \frac{9000 \ln 10 \times {}^2\eta_s^0}{128 \pi^5 n^4 N} J(\bar{\nu}) \qquad (11)$$

$$J(\nu) = \int_0^\infty f_s(\nu)\, \epsilon_a(\nu)\, \frac{d\bar{\nu}}{\bar{\nu}^4}$$

R_0 is related to the second order rate constant for transfer by

$$k_5 = \frac{R_0^3}{(7.35 \times 10^{-8})^3 \tau_s([B] = 0)} \qquad (12)$$

x^2 is an orientation factor equal to 2/3, n is the index of refraction of the solvent, N the Avogadro number, η_s^0 the fluorescence efficiency for [B] = 0, $f_s(\bar{\nu})$ the sensitizer fluorescence distribution (in quanta normalized to unity on a wave number scale), $\epsilon_a(\nu)$ is the molar extinction coefficient (base 10) of the acceptor and $\bar{\nu}$ the wave number. The integrals were evaluated graphically and the η_s^0 values were obtained from the work of Bowen[10] and Melhuish.[13]

Discussion

Figure 2 shows the correlation between the Förster probability integral and the experimental results. It is assumed valid to extrapolate the $1/\tau_s$ vs. [B] plots to calculate the critical concentration where the probability of transfer equals the probability of deactivation by other processes. The relationship between concentration and the average separation $C = 3000/4\pi N R^3$ is also assumed. As indicated in Table II the critical concentration was approached experimentally in some cases. The excited molecules cannot be considered stationary during their lifetime because of the low viscosity of the solvent.

It is frequently argued that complex formation is actually responsible for apparent long range interaction. With regard to the experiments described, this objection can be treated as follows. If an associated system AB formed that was nonfluorescent or of very low fluorescent efficiency, this would not influence the measurements since they are independent of nonfluorescent absorbing substances. If AB did fluoresce, either in the region of B or at a longer wave length, the fluorescence would not pass through the filters and, as a consequence, would not interfere with the measurements. If AB fluoresced in the narrow region of the sensitizer fluorescence band received by the photomultiplier, which is very unlikely, then there would be a mixing of signals. If this were the case and if the efficiency of AB were high, this could influence the measurements. This is extremely unlikely, and it is hard to believe that, if it were true, the $1/\tau_s$ vs. [B] curves would be linear, would extrapolate to the $1/\tau_s$ value for [B] = 0 and, for the series of experiments described, that it would give a series of k_5 values which correlated with the values predicted by the resonance interaction theory.

The maximum second order rate constant for a diffusion controlled collisional deactivation process is approximately $1 \times 10^{10} M^{-1}$ sec.$^{-1}$ for the molecules and solvent in question. Studies carried out in our Laboratory using fluorescence lifetime measurements to determine quenching rate constants for iodide ion quenching of various dyes in

(13) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

TABLE II

EXPERIMENTAL AND CALCULATED RATE CONSTANTS AND CRITICAL DISTANCES

Pair	$C_{m,}{}^a$ mole/liter	$J(\bar{\nu})$	η^0	k_s (eq. 12) M^{-1} sec.$^{-1}$	k_s (exp.), M^{-1} sec.$^{-1}$	R_0, Å (th.)	R_0, Å (exp.)
Anthracene*-perylene	2×10^{-3}	3.94×10^{-14}	0.19^b	2.3×10^{10}	1.2×10^{11}	31	54
Perylene*-rubrene	2×10^{-3}	3.26×10^{-14}	.89	2.8×10^{10}	1.3×10^{11}	38	65
9,10-Dichloroanthracene*-perylene	1×10^{-3}	5.24×10^{-14}	.65	1.7×10^{10}	8.0×10^{10}	40	67
Anthracene*-rubrene	3×10^{-3}	5.38×10^{-15}	.265	7.7×10^{9}	3.7×10^{10}	23	39
9,10-Dichloroanthracene*-rubrene	3×10^{-3}	1.38×10^{-14}	.65	8.5×10^{9}	3.1×10^{10}	32	49

^{a} Maximum concentration of acceptor used in experiments. ^{b} Reduced from 0.265 by self-quenching.

aqueous solution gave values which were within 20% of the theoretical maximum. The self-quenching constants for various polynuclear hydrocarbons derived from Bowen's[10] Stern–Volmer constants with our measured lifetimes approximate the maximum value. Thus, rate constants ranging from 3 to 12 times this value are difficult to explain on any basis other than one involving interaction over distances greater than the average encounter distance. The correlation between the Förster overlap integral and the experimental results furnishes very strong supporting evidence for this explanation. The results are similar to those Bowen and Livingston[4] obtained with the same type molecules and fluorescence intensity measurements.

The phase shift technique is not easily applicable at higher concentrations where departures from Stern–Volmer behavior might be expected. Direct decay measurements[14] as a function of concentration and viscosity would be desirable to test the theory of inverse sixth power dependence of the transfer probability on distance.[15]

As was mentioned above, the self-quenching of anthracene appears to involve a (T/η) independent component with a rather small rate constant of $2.5 \times 10^9 \ M^{-1}$ sec.$^{-1}$. While it is possible that this is due to a resonance transfer of energy, this can hardly be considered adequate evidence. The overlap of the absorption and fluorescence spectra leads to a value for the predicted resonance transfer rate constant of 4×10^9.

While this work was in progress it was reported[16] that the fluorescence efficiency of various polynuclear aromatic hydrocarbons in dilute solution was a function of solvent for a series of aromatic solvents. The solvent quenching efficiency was reported to be in the order benzene < toluene, < xylene, < mesitylene, which is also the order of diminishing ionization energy.

This was checked in the case of anthracene by

(14) R. G. Bennett, Rev. Sci. Inst., 31, 1275 (1960).
(15) B. Ia. Sveshnikov, Soviet Physics Doklady, 2, 336 (1957).
(16) D. K. Majumdar and S. Basu, J. Chem. Phys., 33, 1199 (1960).

measuring both the relative fluorescence efficiency and the lifetime. Both were measured with oxygen-free solutions, and the relative fluorescence efficiency measurements were made with monochromatic excitation at exactly the long wave maximum. It was found that the relative fluorescence efficiency was constant to within the uncertainty of the measurement (5%), and the lifetime was also constant to within 3%. These two independent measurements provide strong evidence that the reported effect does not in fact occur for this particular series of solvents.
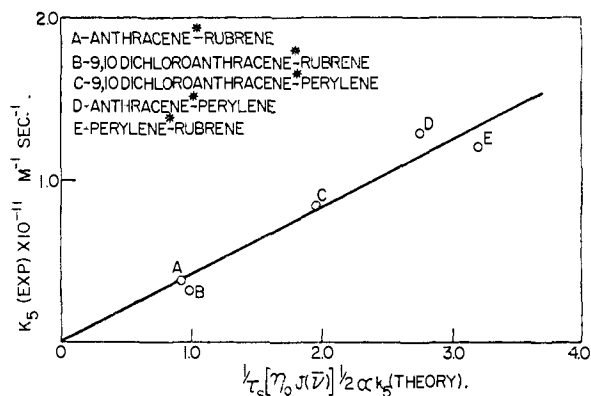

Fig. 2.—Correlation of the observed rate constants with the Förster overlap integral.

Summary.—Resonance transfer of excitation energy between unlike molecules has been examined using fluorescence lifetime measurements. A good correlation has been found between the theoretical predictions for a weak interaction of the allowed dipole type and the experimental rate constants for the process.