uncertainty in the [CH$_3$NO] values as a result of the more extensive deposition of dimer in this run at the higher concentration, may account for the significant difference between the two rates for this experiment.

(b) According to the mechanism I, 1, 2 and 3, the concentration of nitrosomethane at the maximum or plateau region should be related to the absorbed light intensity or azomethane pressure according to (5).

$$[CH_3NO]_{max} = (2I_a\phi_1/k_2)^{1/2} = (aP_{Me_2N_2}/k_2)^{1/2} \quad (5)$$

The near constancy of the ratio $[CH_3NO]_{max}/P_{Me_2N_2}{}^{1/2}$ of column 10 of Table I is consistent with the relation 5. If the destruction of nitrosomethane were first order the function $[CH_3NO]_{max}/P_{Me_2N_2}$, column 9 of Table I, would have been a constant.

The evidence given provides abundant proof of the homogeneity of the reactions of formation and removal of nitrosomethane. The dimer which accumulates on the cell wall is the likely origin of the oxime product which is found under certain conditions. Only in our preliminary experiments with the 1-m. cell (with untreated, chemically reactive walls) was the spectrum of formaldoxime observed as the band of nitrosomethane decayed. Formaldoxime could not be detected in the products from any of the photolyses in the 10-cm. cell or in the long-path cell. It seems well established from our findings and the results of the many previous studies that dimeric nitrosomethane is the major final product of the reaction between methyl radicals and nitric oxide at room temperature under normal experimental conditions. Isomerization of the dimer to the oxime is rapid and the oxime and the products of its decomposition are the dominant products of the reaction when metallic or other reactive surfaces are in contact with the product, when the temperature is above the melting point of the dimers or when water or certain non-aqueous solvents contact the dimer.[8]

Estimate of the Rate Constant for the Homogeneous Dimerization of Nitrosomethane.

—Since no direct observation of the pressure of nitrosomethane monomer present in the reaction mixtures is possible, and the extinction coefficient of nitrosomethane is unknown, an indirect method of estimation of these quantities must be made. It has been established through the azomethane–oxygen mixture photolyses (described in the Results section) that the rate of formation of methyl radicals, which is also equal to the initial rate of formation of CH$_3$NO, is given by

$$(d[CH_3NO]/d)/P_{Me_2N_2} =$$
$$1.66 \times 10^{-8} \text{ mole } CH_3NO/l.\text{-sec.-mm. } Me_2N_2 \quad (6)$$

An average of the most accurate rate data (runs 1, 2 and 3 of Table I) gives

$$(d[\log I_0/I]/dt)/P_{Me_2N_2} =$$
$$0.128 \times 10^{-4} \text{ (sec.-mm. } Me_2N_2)^{-1} \quad (7)$$

Since $\log (I_0/I) = a_M bc$ (where a_M is the molar absorbancy index, b is the path length (10 cm.), and c is the molar concentration), then relation 8 follows

$$(d[\log I_0/I]/dt)/P_{Me_2N_2} = a_M b(d[CH_3NO]/dt)/P_{Me_2N_2} \quad (8)$$

From (6), (7) and (8) we estimate $a_M = 77$ (1./mole-cm.) for the molar absorbancy index of monomeric CH$_3$NO at 6.32μ (resolution, 927; slit width, 56μ). Using this estimate of a_M and the average value of the rate function given in column 8 of Table I, we derive that $k_2 = 87$ (1./mole-sec.) at 25°. Suitable equipment for the determination of k_2 at temperatures other than 25° are not now available to us, so that a measurement of E_2 must be delayed.

Complex Formation in the Flash Photolysis and Combination of Iodine in Benzene[1]

BY S. J. RAND AND R. L. STRONG

The flash photolysis of iodine in liquid benzene at room temperature produces a transient intermediate that absorbs light in the visible region, although no over-all photochemical reaction occurs. It is proposed that this is a complex formed between an iodine atom and a benzene molecule, and the absorption is a charge-transfer spectrum. The disappearance of the complex is second order, consistent with the combination mechanism: $2C_6H_6\cdot I \xrightarrow{k} C_6H_6\cdot I_2(+C_6H_6)$. Values of k/ϵ_c where ϵ_c is the molar extinction coefficient of the complex, are independent of initial iodine concentration (0.65 to 5.5 $\times$ 10^{-5} M). An IBM-650 digital computer has been used to calculate values of k and ϵ_c for various assumed values of the primary quantum yield of dissociation of iodine in benzene.

Introduction

The combination of iodine atoms in several "inert" solvents has been studied by the flash photolysis technique[2-4] and by the allyl iodide and oxygen scavenger technique combined with rotating sector measurements.[5,6] The primary quantum yield of dissociation ϕ, defined for these systems as the quantum yield for producing a pair of atoms that escape from each other and ultimately combine with atoms from other dissociations,[6]

(1) Presented at the 135th meeting of the American Chemical Society, Boston, Massachusetts, April, 1959.

(2) R. Marshall and N. Davidson, J. Chem. Phys., 21, 2086 (1953).

(3) R. L. Strong and J. E. Willard, THIS JOURNAL, 79, 2098 (1957).

(4) S. Aditya and J. E. Willard, ibid., 79, 2680 (1957).

(5) F. W. Lampe and R. M. Noyes, ibid., 76, 2140 (1954).

(6) H. Rosman and R. M. Noyes, ibid., 80, 2410 (1958).

is less than unity because of the "cage" of solvent molecules that results in some recombination into the original molecule. The rate of combination is determined by the diffusion together of the atoms.

The spectra of iodine in benzene and other aromatic hydrocarbons have been studied in detail[7] and interpreted in terms of the formation of a complex between the molecular iodine and the aromatic molecule. Mulliken[8] has presented a quantum-mechanical theory for this interaction in terms of an intermolecular transfer of charge from the aromatic (donor) to the I_2 (acceptor), which predicts a strong absorption spectrum in the near ultraviolet that is characteristic of neither the acceptor nor the donor alone. Similar complexes exist with Cl_2[9] and Br_2,[10,11] among others, serving as acceptor molecules.[12]

Russell[13] has proposed the existence of a complex formed by the association of a chlorine atom with the π-electrons in aromatic solvent molecules to explain the reduced reactivity, and thus greater selectivity, in various photo-chlorination reactions. Hoare and Walsh[14] present the formation of a charge-transfer complex between an iodine atom and various aromatic molecules or I_2 as a possible explanation for the greater efficiency of these molecules as third bodies in the gas-phase atom combination reactions. A similar suggestion has been made by Basila,[15] who has shown that the rate of iodine atom combination increases with different aromatic (and I_2) molecules with increasing stability of the corresponding charge-transfer complex involving I_2 molecules. The possibility of a charge-transfer complex between a halogen atom and its molecule (serving as a third body) provides an explanation for the much greater efficiency of I_2 as a third body relative to Br_2[15,16] because of the greater ionization potential of Br_2. In this paper spectral evidence is presented for the transient formation of an I atom–benzene charge-transfer complex during the flash photolysis and combination of iodine in benzene.

Experimental

Flash Apparatus[17].—The flash apparatus was similar to the apparatus used by Strong, et al.[18] It consisted of a flash lamp having four quartz discharge tubes, each containing aluminum electrodes 12 cm. apart, arranged in cylindrical form with an inside diameter of 8 cm. and an over-all length of 40 cm. The lamp was mounted on an optical bench and surrounded by a cylindrical polished aluminum reflector.

(7) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

(8) R. S. Mulliken, ibid., **74**, 811 (1952), and subsequent papers of this series.

(9) L. J. Andrews and R. M. Keefer, ibid., **73**, 462 (1951).

(10) N. W. Blake, H. Winston and J. A. Patterson, ibid., **73**, 4437 (1951).

(11) R. M. Keefer and L. J. Andrews, ibid., **72**, 4677 (1950).

(12) L. J. Andrews, Chem. Revs., **54**, 713 (1954).

(13) G. A. Russell, THIS JOURNAL, **77**, 4031 (1955).

(14) D. E. Hoare and A. D. Walsh, Chem. Soc. Spec. Publ., **9**, 17 (1957).

(15) M. R. Basila, Ph.D. dissertation, Rensselaer Polytechnic Institute, 1958, available from University Microfilms, Ann Arbor, Michigan.

(16) W. G. Givens and J. E. Willard, THIS JOURNAL, **81**, 4773 (1959).

(17) The construction and operation of the particular flash apparatus used in this work are described in detail in ref. 15.

(18) R. L. Strong, J. C. W. Chien, P. E. Graf and J. E. Willard, J. Chem. Phys., **26**, 1287 (1957).

The reaction cell (described below) was placed in the center of the flash lamp along its cylindrical axis. All determinations were made with the reaction cell wrapped with an Eastman Kodak K2 (yellow) gelatin Wratten filter (cutoff at approximately 4700 Å.) to prevent flash light absorption by the I_2-benzene charge-transfer complex.

The continuous analyzing beam, from a prefocussed automobile head lamp operated off two 6.3 volt storage batteries connected in parallel, was rendered approximately monochromatic by the appropriate Bausch and Lomb interference filter (half-band width approximately 80 Å.) and a Corning 3850-051 filter to cut off the secondary pass band in the ultraviolet. Changes in light intensity were detected by a 931-A photomultiplier tube, and the resulting signal was amplified, clipped (to prevent overloading of the oscilloscope) and fed through a cathode follower amplifier to a Tektronix type 531 oscilloscope equipped with a type 53B plug-in preamplifier. The oscilloscope tracing, which records the voltage due to the change in light intensity as a function of time, was photographed. The steady intensity of the analyzing beam was recorded by a Leeds and Northrup Speedomax type G recorder.

The flash lamp was fired by applying a positive pulse from the gate-out of the oscilloscope to the grid of a General Electric GL 5380/5G41 mercury thyratron tube. The ionization time of the thyratron (about 20 microseconds) was sufficient to give a starting point on the oscilloscope screen. The flash for a capacitance of 30 microfarads, 7000–8000 volts, reached its maximum intensity in about 40 microseconds and decayed exponentially with a half-time of 20 microseconds (Fig. 1).

Purification of Materials and Filling of Cells.—The cylindrical reaction cells were made of Pyrex with optically flat windows. They were 10 cm. long (light path) and 2.8 cm. o.d. with two side arms perpendicular to the cylindrical axis (total volume approximately 53 ml.). The reaction cells and other glass apparatus that contained the iodine and the benzene were cleaned with fuming nitric acid at a temperature of 55–60°, washed and dried. The walls were degassed by flaming before the reactants were introduced when filling was done on a vacuum system.

Thiophene-free benzene (Fisher certified reagent) was further purified by dissolving in it a small amount of resublimed iodine and illuminating for approximately 24 hr. with a 500 watt tungsten lamp. The iodine was removed by extraction with 0.02 M Na_2SO_3 followed by repeated washing, and the benzene was distilled quickly over P_2O_5, refluxed over sodium ribbon for several hours, and then distilled over sodium, only the middle fraction being used. After the purified benzene was poured into a reservoir on the vacuum system and frozen out at Dry Ice temperature, dry air was drawn over the solid benzene while the filling tube was sealed, to prevent pyrolysis of the benzene. It then was degassed in vacuo, and the proper amount was transferred to a calibrated freeze-out trap connected to the reaction cell. Resublimed iodine (Fisher certified reagent) was ground with KI, distilled on the vacuum system through a P_2O_5 drying tube and degassed. The desired amount of iodine was metered into the same trap on the cell by allowing the solid iodine to equilibrate with its vapor at a constant temperature into a known volume.

The freeze-out trap and the reaction cell were sealed off from the vacuum system. The solution of iodine and benzene, after being warmed to room temperature, was allowed to drain completely into the reaction cell, and a solid plug was formed by freezing some of the solution with liquid nitrogen in a small U-tube between the reaction cell and the freeze-out trap. The trap and the reaction cell then were separated by sealing off.

Two reaction cells were filled in air. These were fitted with ground glass caps on the side arms, and the benzene and iodine were purified as described above.

The iodine concentration of each cell was determined spectrophotometrically on a Beckman model DU spectrophotometer after they had been prepared, using a value of 1040 for the molar extinction coefficient at 5000 Å.[7]

The absorbancy of each cell was determined both before and after a series of flash photolysis experiments; the difference was always less than 0.5%, indicating no over-all reaction had occurred. Each cell gave reproducible results for a period of one to two months after its preparation; however, its absorption then began to increase over the whole
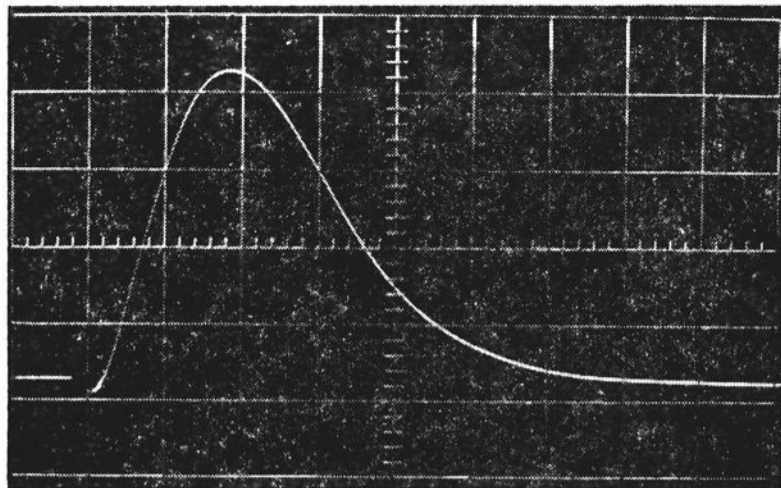
Fig. 1.—Oscillogram of flash light intensity. Horizontal sweep time equals 20 μsec. per major division.

spectrum and solid particles began to form in the cell. The solution then was discarded.

One reaction cell was filled by putting sodium ribbon into the benzene reservoir on the vacuum system in order to take out any water vapor that might have been introduced when the benzene was poured into the reservoir. Determinations with this cell gave results that did not differ from those of other cells which may have contained a small amount of water vapor.

Results

The absorption of light after the dissociation of iodine in benzene by flash photolysis has been followed as a function of time at 4200, 4900 and 6000 Å. At all three wave lengths a decrease in transmittancy occurred during the short time of the flash (which could not be measured with any accuracy because of scattered light from the flash and stray electrical and magnetic interference) followed by the return of the transmittancy to its value prior to the flash in less than five milliseconds. Oscillograms are shown in Fig. 2 for a typical run at 4200 Å., where there is little absorption by iodine or the molecular iodine–benzene complex.[7] The observed changes were small—usually less than 1% maximum—so that the change in transmittancy may be taken as directly proportional to the concentration of the transient, absorbing species, assuming that Beer's law holds.

Figure 3 is a plot of the reciprocal of the change in transmittancy *versus* time at 4200 Å. The linearity of this plot over a 5-fold change in concentration clearly demonstrates a second-order disappearance of the absorbing species. This would seem to rule out the possibility of excited molecule formation, as its disappearance in the presence of a large excess of solvent molecules would be expected to be apparent first order.

Consistent with these observations, it is proposed that a complex is formed between an iodine atom and a benzene molecule following photolysis of the I_2, and the absorption in the visible region is a charge-transfer spectrum of the complex.[8] Disappearance of the complex occurs by the second-order mechanism

$$2C_6H_6\cdot I \xrightarrow{k} C_6H_6\cdot I_2 \ (+C_6H_6) \qquad (1)$$
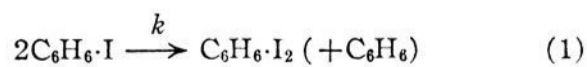
$$-\frac{d[C_6H_6\cdot I]}{dt} = 2k[C_6H_6\cdot I]^2 \qquad (2)$$

(The product of the combination is written as the iodine molecule–benzene complex, although only about 60% of the I_2 molecules presumably are in this form.)
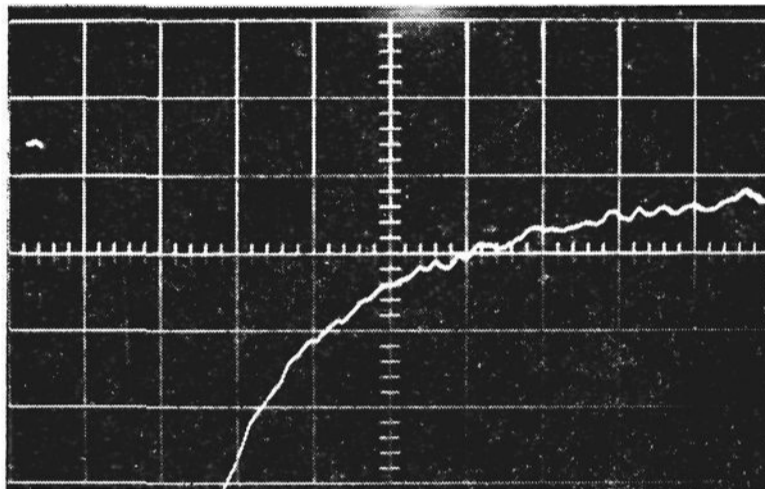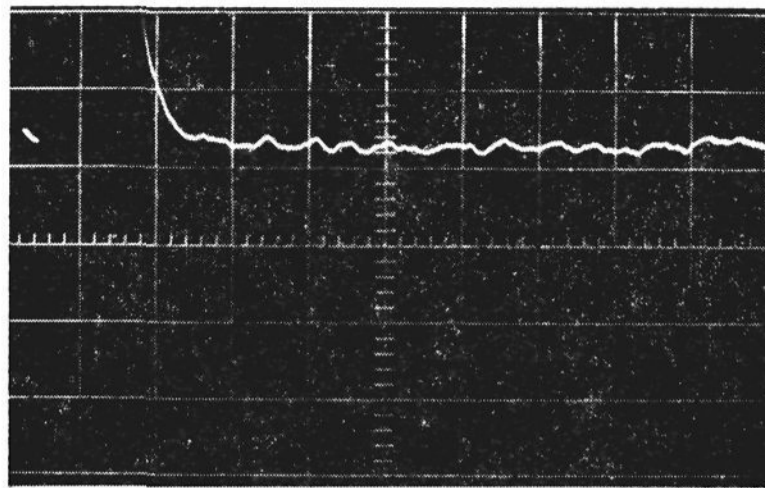

Fig. 2.—Oscillograms showing the transient decrease in transmittancy at 4200 Å. following flash photolysis of iodine in benzene. Upper oscillogram: scattered light, etc., from pure benzene cell. Lower oscillogram: deflection for a cell containing 2.7×10^{-5} mole/l. I_2 in benzene. Sweep time equals 100 microseconds per major division; vertical scale corresponds to decrease in transmittancy equal to *ca.* 0.05% per small division, although correction has to be applied to allow for non-linearity of amplifier and clipper circuits.
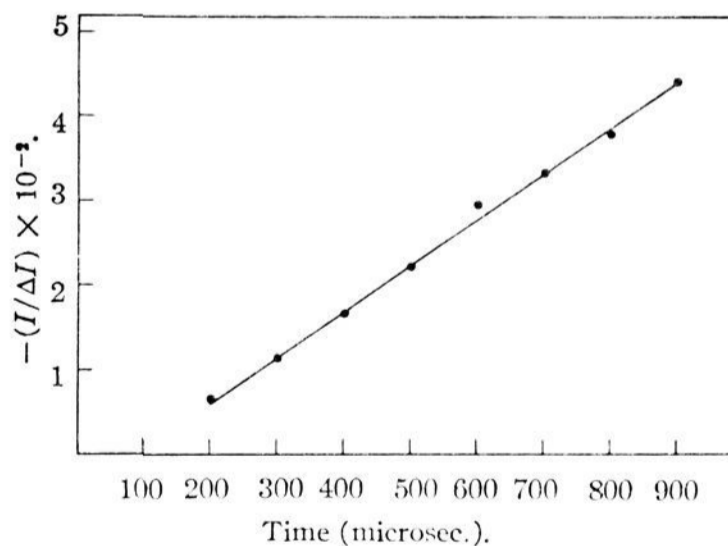

Fig. 3.—Reciprocal of change in transmittancy *vs.* time, wave length = 4200 Å.

Because the complex exists only as a transient intermediate, it is not possible to measure or estimate its concentration without knowledge of ϕ and the stability of the complex (as discussed below), and therefore the combination rate constant k cannot be calculated. However, the product of the molar extinction coefficient ϵ_c and the complex concentration can be measured, for

$$\epsilon_c[C_6H_6\cdot I] = (1/d) \log (I_0/I) \qquad (3)$$

where d is the cell light path and log (I_0/I) is the measured absorbancy. Values of k/ϵ_c were calculated from the integrated form of (2) and are given in Table I for various initial I_2 concentrations at 4200 Å. The results at each concentration represent at least 15 separate determinations, with a standard deviation of $\pm 8\%$.

TABLE I

SUMMARY OF RESULTS ON THE DISAPPEARANCE OF COMPLEX FOLLOWING FLASH PHOTOLYSIS OF IODINE IN BENZENE

Cell[a]	Wave length, 4200 Å. $[I_2]_0 \times 10^5$ (mole/l.)	$(k/\epsilon_c) \times 10^{-6}$ (cm./sec.)
E	0.65	7.3
F	2.98	7.6
G	5.47	7.1
H	3.24	7.9
J	3.66	7.2
A-2[b]	2.77	6.3
A-3[b,c]	3.32	5.9

[a] All cells wrapped with Wratten K_2 (yellow) gelatin filter, so that photolyzing flash light limited to wave lengths greater than 4700 Å. [b] Cells A-2 and A-3 filled in air; others filled in vacuo. [c] Capacitors discharged at 8000 volts; other runs at 7000 volts.

Within the limit of experimental error, values of k/ϵ_c are independent of initial I_2 concentration (0.65 to 5.47 mole/l.) for the cells filled in vacuo. Values of k/ϵ_c for the two air-filled cells, while consistent within themselves, are significantly lower than the average of the air-free cells. It is possible that this is a perturbation of the charge-transfer spectrum (and hence ϵ_c) by the paramagnetic property of the oxygen molecule; a similar perturbation has been observed in the singlet-triplet absorption spectra of aromatic hydrocarbons.[19] It should be noted, however, that the concentration of O_2 dissolved in benzene in equilibrium with air is approximately 50 times that of the I_2 used, and oxygen is also believed to form a charge-transfer complex with benzene.[20] As shown below, the presence of air has little effect, if any, on relative values of ϵ_c at various wave lengths.

Estimation of k and ϵ_c.—During the lifetime of the flash (of the order of 120 microseconds), $C_6H_6 \cdot I$ complexes are simultaneously being produced by photolysis of I_2 and disappearing by combination. The complete rate expression, assuming as above that all iodine atoms that escape parent recombination are complexed, is given by

$$\frac{d[C_6H_6 \cdot I]}{dt} = 2\phi I_a - 2k[C_6H_6 \cdot I]^2 \qquad (4)$$

The light absorbed (I_a, in quanta cc.$^{-1}$ sec.$^{-1}$) varies with time but is directly proportional to the intensity of the flash lamp (shown in Fig. 1 as a function of time) provided the per cent. absorbed by the cell is small. The peak absorption of light (at 40 microseconds) for a given system can be calculated using the method of Strong and Willard[3] with an I_2–argon gas cell as an actinometer.

Equation 4 cannot be integrated to give k because neither ϕ nor $[C_6H_6 \cdot I]$ is known, although the quantity $k \times [C_6H_6 \cdot I]$, equal to k/ϵ_c times $\epsilon_c[C_6H_6 \cdot I]$, can be calculated at a specific time after the flash light intensity has decayed to a negligible

value. Using the fourth-order method of Runge and Kutta[21] and the aid of an IBM-650 digital computer, equation 4 has been solved for given values of ϕ, ranging from 0.1 to a maximum of unity, from the experimentally determined boundary conditions at 300 microseconds. Resulting values of k, ϵ_c and $[C_6H_6 \cdot I]$ at 300 microseconds are listed in Table II for cell H (initial I_2 concentration: 3.24×10^{-5} mole/l.).

TABLE II

CALCULATED VALUES OF THE RATE OF COMBINATION, EXTINCTION COEFFICIENT AND COMPLEX CONCENTRATION FOR ASSUMED VALUES OF THE PRIMARY QUANTUM YIELD

Wave length = 4200 Å.

ϕ	$k \times 10^{-11}$ (l. mole^{-1} sec.$^{-1}$)	ϵ_c (l. mole^{-1} cm.$^{-1}$)	$[C_6H_6 \cdot I] \times 10^8$ (moles/l.) at $t = 300$ μsec.
1.0	1.02	12,900	2.6
0.9	1.15	14,500	2.3
.8	1.33	16,800	2.0
.7	1.51	19,100	1.7
.6	1.75	22,200	1.5
.5	2.12	26,800	1.3
.4	2.60	32,900	1.0
.3	3.50	44,300	0.8
.2	5.20	65,800	.5
.1	10.4	132,000	.3

These results are subject to considerable uncertainties which are difficult to evaluate, however, because the computer integration is extremely sensitive to errors in I_a and $\epsilon_c[C_6H_6 \cdot I]$. As these in turn each depend on single point measurements (I_a on the extrapolated value of $I/\Delta I$ to zero time for an I_2–argon gas cell, and $\epsilon_c[C_6H_6 \cdot I]$ on the oscilloscope deflection at 300 microseconds), they are in greater error than the k/ϵ_c values, which are calculated from the slopes of many points. Thus, while the changes in k and ϵ_c with varying ϕ are certainly significant, the absolute values given in Table II are qualitative only.

Comparison of ϵ_c at 4200, 4900 and 6000 Å.—The highest concentration that $C_6H_6 \cdot I$ can have is when ϕ is unity, and this is of the order of 2.6 $\times$ 10^{-8} mole/l. at 300 microseconds (Table II). Thus, assuming that all iodine atoms not complexed are present as I_2 (or $C_6H_6 \cdot I_2$), more than 99.95% of the atoms are in the molecular form. At 4900 Å., where the absorption by molecular iodine is close to its maximum value,[7] this 0.05% change in I_2 concentration after 300 microseconds would result in a change in transmittancy corresponding to an oscilloscope deflection of less than one-half of one small division (Fig. 2), which is within the experimentally observed fluctuations resulting from shot noise and stray transient pickup. (At other wave lengths the deflection will be even less.) Therefore, observed changes in transmittancy are presumed to be due to changes in $C_6H_6 \cdot I$ concentration alone. This makes possible a comparison of the molar extinction coefficients at various wave lengths from calculated k/ϵ_c values, as given in Table III for four cells that were analyzed at 4200 and 4900 Å.

(19) D. F. Evans, J. Chem. Soc., 1351 (1957).

(20) D. F. Evans, ibid., 345 (1953).

(21) W. E. Milne, "Numerical Solution of Differential Equations," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 72–73.

TABLE III

RELATIVE VALUES OF THE MOLAR EXTINCTION COEFFICIENT
OF $C_6H_6 \cdot I$ AT 4200 AND 4900 Å.

$(k/\epsilon_c) \times 10^{-6}$ (cm./sec.)

Cell	4200	4900	$\epsilon_{c_{4200}}/\epsilon_{c_{4900}}$
E	7.3	3.7	0.51
F	7.6	3.9	.51
G	7.1	3.5	.50
A-3	5.9	3.1	.53

A very small deflection was also measured at 6000 Å. indicating slight absorption by the complex at this wave length but was too small to permit the accurate calculation of k/ϵ_{c6000} after the deflections were corrected for stray light of other wave lengths transmitted by the filter.

Discussion

The calculated extinction coefficients in Table II, although large, are to be expected from Mulliken's theory of intermolecular charge-transfer interaction.[8] The several simplifications of the theory[22,23] used to explain certain regularities between the ionization potential of the donor molecules and the observed maximum of the charge-transfer spectrum involving molecular iodine should not hold with this system because the constants involved are considerably different for different acceptors.[24] Qualitatively, though, the complex involving I atoms might be expected to be more stable than the corresponding I_2 complex because of the larger electron affinity of the I atom, so that ϵ_{max} should shift toward longer wave lengths. The data of Table III and the observed very slight absorption at 6000 Å., admittedly very scanty, suggest that a maximum exists between 4000 and 5000 Å. This shift is quite large compared to that of only 200 Å. for quite different acceptor molecules.[22]

(22) H. McConnell, J. S. Ham and J. R. Platt, J. Chem. Phys., 21, 66 (1953).

(23) S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, 75, 2901 (1953).

(24) R. S. Mulliken, Rec. trav. chim., 75, 845 (1956).

Increased stability of the complex theoretically should also lead to an increase in the intensity of the charge-transfer spectrum, although the results of Benesi and Hildebrand[7] indicate that ϵ_{max} decreases with increasing complex stability in the methylated benzene series. (Orgel and Mulliken,[25] however, have suggested that the observed intensities are composed of both "contact" and "complex" charge-transfer spectra. When an appropriate division is made between the two possibilities, an increase in ϵ_c with increasing complex stability can be calculated.) Thus the values given in Table II for ϵ_c are reasonable, especially at the larger values of ϕ, even though 4200 Å. is obviously not the wave length of maximum absorption.

Even the smallest possible value for the rate of complex combination ($i.e.$, 1.02×10^{11} l. mole^{-1} sec.$^{-1}$, when $\phi = 1$) is about 18 times larger than the recombination of iodine atoms in carbon tetrachloride.[3] This is surprising, for if the rate of combination is diffusion-controlled as presumed[6] then k should be $smaller$ for the complexed atom (with its larger diffusion diameter) than for the free atom. The fact that both ϵ_c and k are large at $\phi = 1$, and increase markedly to unreasonable values with decreasing ϕ, supports the view that the formation of the complex stabilizes the I atoms so that most of them escape recombination into the parent molecule in contrast to the caging effect and low degree of dissociation of I_2 in inert solvents.

(25) L. E. Orgel and R. S. Mulliken, THIS JOURNAL, 79, 4839 (1957).

TROY, NEW YORK

[CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY, E. I. DU PONT DE NEMOURS & COMPANY]

Kinetics and Mechanisms for the Oxidation of Trivalent Plutonium by Nitrous Acid[1]

BY E. K. DUKES

The rate of oxidation of plutonium(III) by nitrous acid was investigated in nitric, hydrochloric and perchloric acids. The rate expressions obtained were in HCl or $HClO_4$, $- d[Pu(III)]/dt = K_1[Pu(III)][H^+][HNO_2]$; in HNO_3, $- d[Pu(III)]/dt = K_2[Pu(III)][H^+][NO_3^-][HNO_2]$ where $K_1 = 18 \pm 3.5$ moles^{-2} min.$^{-1}$ and $K_2 = 90 \pm 20$ moles^{-3} min.$^{-1}$. The proposed mechanisms for the oxidation of Pu(III) by nitrous acid involve N_2O_4 as an intermediate in HNO_3 and NO^+ as an intermediate in HCl or $HClO_4$. Activation energies of 14.0 ± 0.5 and 6.0 ± 0.3 kcal./mole were found for K_1 and K_2. Studies were made with solutions 10^{-5} to 10^{-6} molar in plutonium and the change in distribution coefficient of plutonium into 30 vol. % tributyl phosphate (TBP) was used to follow the reaction.

Introduction

Nitrous acid oxidizes trivalent plutonium to tetravalent plutonium in acid solutions by the

reaction

$$Pu(III) + H^+ + HNO_2 \longrightarrow Pu(IV) + NO + H_2O$$
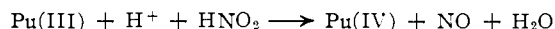
The rate of this reaction is measurable at tracer concentrations of Pu but no data have been published. This paper reports the results of a study of the