Yields of Radical Ions in the Pulse Radiolysis
of Liquid Cyclohexane Solutions

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Experiments have been performed to measure the yields of ions on radiolysis of a liquid hydrocarbon. Pulse radiolysis of nine different aromatic solutes in cyclohexane gave rise to transient spectra, some of which could be assigned to aromatic radical ions. It was not possible to distinguish whether the ion absorptions were due to anions or cations. Total radical ion yields were obtained using literature values for the extinction coefficients of anion or cation (assumed to be equal). For all the solutes used the sum of anion and cation yields at concentrations up to 10^{-1} M were less than or equal to 0.6. These yields are consistent with those found in most previous experiments by other workers using different methods but are much lower than the yields implied by using N_2O as an electron scavenger. It may be that some of the ion pairs formed by radiation recombine in times much less than a microsecond. Such ions are not detected by pulse radiolysis or conductivity measurements, but in the N_2O experiments recombination is accompanied or preceded by measurable chemical effects.

Introduction

Until recently it has been possible to interpret the formation of many of the products in the radiolysis of liquid hydrocarbons and their mixtures in terms of the reactions of neutral free radicals and other uncharged species.[1] Support for this interpretation is found in the low separated ion-pair yields of ~0.1–0.25 found in electrical conductivity measurements on irradiated hexane[2] and cyclohexane.[3] However, experiments with N_2O have suggested that the reactions of electrons may be playing an important part,[4] and work with pulse radiolysis has provided qualitative confirmation.[5] Similarly, experiments with solid solutions in hydrocarbons[6] provide strong indications that significant yields of radical ions may be present. Quantitative information is now presented on the formation of radical ions in the pulse radiolysis of cyclohexane containing various solutes.

Experimental Section

The cyclohexane used (B.D.H. spectroscopic grade) was passed through an activated silica gel column and then distilled *via* a fractionating column, the middle fraction being used. The solutes used were the purest commercially available, being of either Analar or

microanalytical reagent quality. All solutions, unless otherwise stated, were deoxygenated by bubbling with argon for at least 1 hr. The argon contained <6 p.p.m. oxygen and was supplied by the British Oxygen Co. The nitrous oxide used was supplied by the same company. Details of the pulse radiolysis apparatus have been published elsewhere.[7] Samples (1.5 ml.) of the experimental solution were irradiated in a fused silica cell, path length 1.62 cm., with single 2.0-μsec. pulses of 4-Mev. electrons. Doses, which were up to 8000 rads, were measured with a secondary emission chamber which had been calibrated with the modified Fricke dosimeter consisting of 10^{-2} M $FeSO_4$ in 0.8 N H_2SO_4, saturated with oxygen.[8] The extinction coefficient of ferric ion at 3040 Å. was taken to be 2097 ± 3 at 20°, and a $G(Fe^{3+})$ value of 15.42 ± 0.04 was used.[9] The dose received by cyclohexane as compared with aqueous ferrous sulfate solution was assumed to be in the ratio of the electron densities of the two liquids. Values of dose thus obtained were estimated to be accurate to within ±5%. The optical transmission of the irradiated solution before and after a pulse was presented as a function of time on the screen of a cathode ray oscilloscope. For the measurement of spectra, deflections at a particular time after the pulse were noted. In most cases the spectrum was measured immediately (~1 μsec.) after the pulse. Wave length maxima were estimated to the nearest 50 Å. When kinetic data were required, the whole trace was photographed and measurements were made from the photograph.

The absorbing species often decayed completely within 5–10 μsec. In order to estimate the G value for radical ions, it was necessary to correct the measured optical density for decay during the pulse. This could not be done very accurately since the decay of the active species often fitted neither first-order (log O.D. ∝ time) nor second-order (1/O.D. ∝ time) kinetics. Accordingly, both plots were drawn and the one giving the best straight line over the first few microseconds was used for extrapolation. Corrections obtained in this way were in the range 30 to 120%.

Results

Pulse radiolysis of pure cyclohexane has been shown to give rise to a weak transient absorption around 2500 Å.[10] (attributed to the cyclohexyl radical) and no other absorptions in the range 2300–7500 Å. In the present experiments, using nine different aromatic solutes in cyclohexane, new transient spectra were observed on pulse radiolysis using doses of ~7000 rads

(1) A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, New York, N. Y., 1960.

(2) A. O. Allen and A. Hummel, *Discussions Faraday Soc.*, **36**, 95 (1963).

(3) G. R. Freeman, *J. Chem. Phys.*, **39**, 988 (1963).

(4) G. Scholes and M. Simic, *Nature*, **202**, 895 (1964).

(5) G. Scholes, M. Simic, G. E. Adams, and J. W. Boag, *ibid.*, **204**, 1187 (1964).

(6) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

(7) J. P. Keene, *J. Sci. Instr.*, **41**, 493 (1964).

(8) J. K. Thomas and E. J. Hart, *Radiation Res.*, **17**, 408 (1962).

(9) J. P. Keene and J. Law, *Phys. Med. Biol.*, **8**, 83 (1963).

(10) M. Ebert, J. P. Keene, E. J. Land, and A. J. Swallow, *Proc. Roy. Soc.* (London), A287, 1 (1965).

(Figure 1). The solutes were chosen because they could give rise to radical ions with known absorptions.[11–15] The change with time of the optical density at the various peaks is given in Figure 2. In most cases the decay rates did not fit first- or second-order kinetics.

In the case of benzophenone, the two distinct regions of absorption in the range 4500–8000 Å. (Figure 1a) are in agreement with previous studies.[5,16] The initial height of the $\sim$7000-Å. peak was studied as a function of benzophenone concentration over the range 10^{-4}–10^{-1} M. The results obtained are shown in Table I, together with those for anthracene at 7200 Å. over a concentration range 3×10^{-6}–10^{-2} M. Saturation with nitrous oxide instead of argon reduced the optical densities observed at $\sim$7200 Å. using 10^{-2} and 10^{-4} M anthracene by 72 and 65%, respectively.

Table I. Heights of Peaks at $\sim$7000 and $\sim$7200 Å. Obtained on Pulse Radiolysis of Benzophenone and Anthracene, Respectively, as a Function of Solute Concentrations[a]

Solute concn., M	Optical density[b]	
	$\sim$7000 Å. (benzophenone)	$\sim$7200 Å. (anthracene)
3×10^{-6}	. . .	0.0043
10^{-5}	. . .	0.0133
3×10^{-5}	. . .	0.0146
10^{-4}	0.0049	0.0149
3×10^{-4}	0.0110	0.0210
10^{-3}	0.0125	0.0205
3×10^{-3}	0.0132	0.0194
10^{-2}	0.0124	0.0205
3×10^{-2}	0.0139	. . .
10^{-1}	0.0158	. . .

[a] The dose per pulse was normalized to 5000 rads, and the monochromator band width was 200 Å. [b] Corrected for decay during pulse.

For the 10^{-2} M biphenyl solution, the two peaks in the range 3000–8000 Å. (Figure 1c) are in agreement with previous studies of this system.[5] The maximum transient optical density at 6600 Å. was also measured for 10^{-1} M biphenyl, a density of 0.022 being obtained for a dose of 5000 rads. The decay of this absorption followed second-order kinetics, $k/\epsilon = 6 \times 10^7$ cm. sec.$^{-1}$.

A 10^{-2} M solution of nitrobenzene gave a transient spectrum with two maxima in the range 2500–6000 Å. (Figure 1d). In addition, a very long-lived new absorption, stable for >1 msec., was also noted with a maximum at $\sim$3000 Å.

A 10^{-3} M solution of styrene gave a spectrum containing two peaks in the range 3600–6000 Å., one short-lived and the other stable for >50 msec. (Figure 1e). The decay was measured of the species absorbing at the longer wave length (Figure 2e) and was found to give a good second-order plot $k_{II}/\epsilon_{4200Å}$. being 7×10^7 cm. sec.$^{-1}$, estimated error $\pm 10\%$.

(11) E. J. Land, Progr. Reaction Kinetics, 3, 369 (1965).
(12) G. Porter and F. Wilkinson, Trans. Faraday Soc., 57, 1686 (1961).
(13) G. J. Hoijtink and P. J. Zandstra, Mol. Phys., 3, 371 (1960).
(14) K. H. J. Buschow, J. Dielman, and G. J. Hoijtink, Mol. Phys., 7, 1 (1963).
(15) E. J. Land, Ph.D. Thesis, University of Sheffield, 1962.
(16) F. S. Dainton, T. J. Kemp, G. A. Salmon, and J. P. Keene, Nature, 203, 1050 (1964).

Discussion

Assignment of Transients. The dashed curves in Figure 1 show the known spectra of some radical ions[12–15] on an arbitrary scale. Comparison of these spectra with the spectra obtained on pulse radiolysis of the corresponding solute in cyclohexane suggests that some radical-ion formation occurs on pulse radiolysis. It has been predicted theoretically[17] that the spectra of corresponding aromatic radical anions and cations should be almost the same. This has been confirmed experimentally in a few cases.[17] Any differences occurring are probably too small to be detected by the present optical arrangement so that it is not possible from the evidence available at present to distinguish between anions and cations. In the present work, radical anions might be formed by electron capture and radical cations by positive charge transfer.

(*a*) *Benzophenone.* It is apparent from the decay curves shown in Figure 2a for a 10^{-2} M solution that the 5400- and $\sim$7000-Å. bands belong to separate species. The strong peak at 5400 Å. corresponds well with the known absorption spectrum of the neutral ketyl radical. However, triplet–triplet (T–T) absorption of benzophenone[16] occurs at the same wave length and so it also probably contributes to the absorption observed at 5400 Å. The broad band with a maximum near 7000 Å. is consistent with the absorption spectrum of the ketyl anion $(C_6H_5)_2CO^-$, which has been measured in 50 vol. % 2-propanol–water mixture[12] (Figure 1a). The difference between the two maxima is probably due to a solvent shift.

(*b*) *Anthracene.* The steeply rising absorption in the region of 4250 Å. is likely to be due to T–T absorption of anthracene. The weaker, shorter-lived absorption with peak around 7300 Å. is consistent with the spectrum of the anthracene radical anion. This has been shown[13] to have a structured peak around 7000 Å. in 2-methyltetrahydrofuran glass (Figure 1b). Signs of structure were also noticed in the longer wave length band obtained on pulse radiolysis, particularly for 10^{-4} M anthracene. Addition of a large excess of N_2O ($\sim$2 $\times$ 10^{-1} M), an efficient electron scavenger, to 10^{-4} M anthracene in cyclohexane reduced the radical ion absorption by 65%. This could be taken as evidence that the remaining absorption is due to the anthracene radical cation alone. A similar reduction in radical-ion absorption in the presence of N_2O has been observed for biphenyl in cyclohexane.[5]

(*c*) *Biphenyl.* The T–T absorption spectrum of biphenyl has absorption maxima at 3685 and 3520 Å.,[18] and so the $\sim$3700-Å. peak observed on pulse radiolysis is attributable partly to the triplet state. The biphenyl radical anion in 2-methyltetrahydrofuran glass has a weak absorption band at 6400 Å. and a stronger one at 4100 Å.[14] (Figure 1c). The short-lived absorption at about 6500 Å. observed on pulse radiolysis is therefore attributable to a biphenyl radical ion. The stronger absorption of the ion at 4100 Å. shows up as a shoulder at this wave length in the pulse-radiolysis-produced spectrum.

(17) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963, Chapter 12.
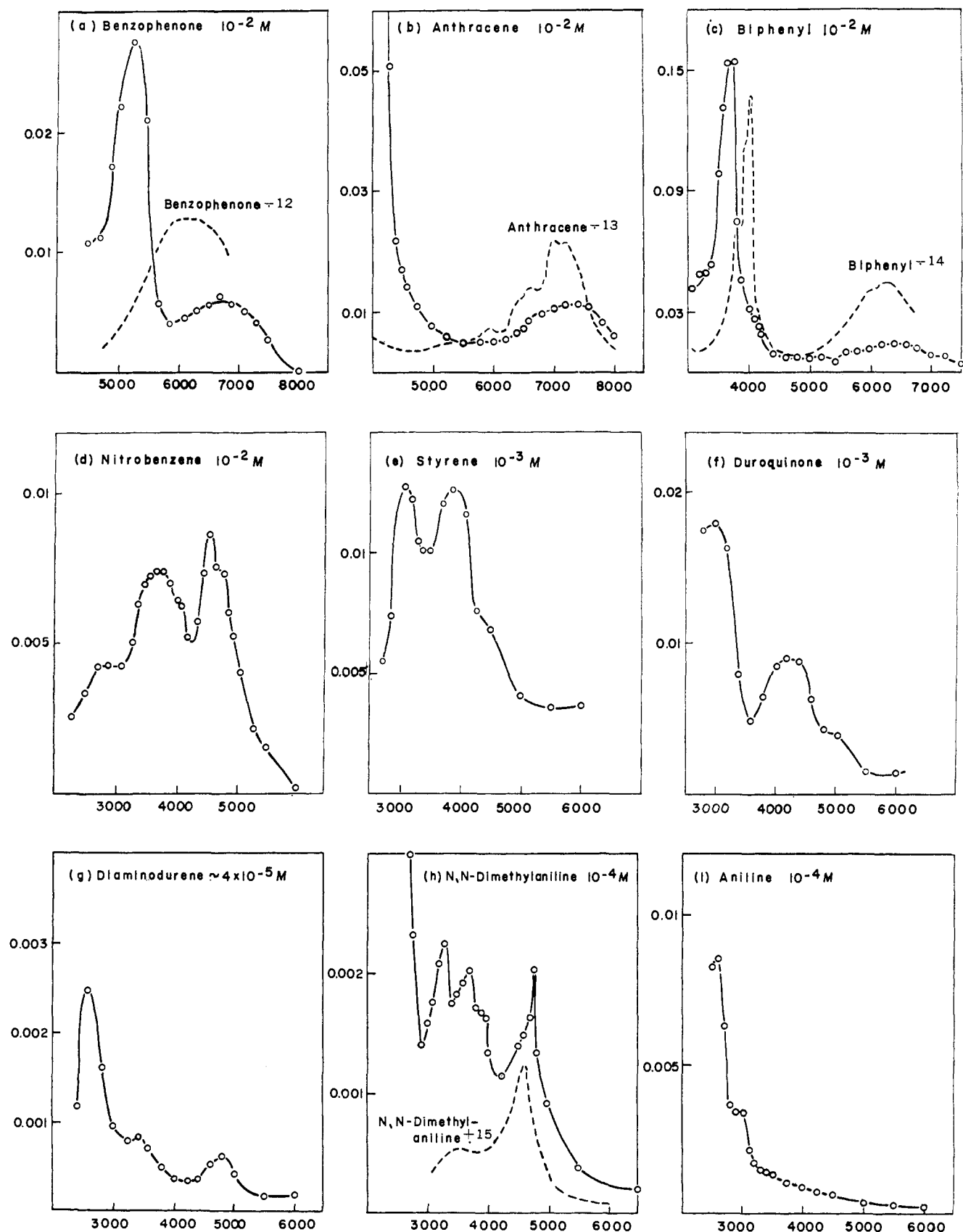(18) G. Porter and M. W. Windsor, Proc. Roy. Soc. (London), A245, 238 (1958).

Figure 1. Absorption spectra of cyclohexane containing various solutes immediately after a 2-μsec. pulse of 4-Mev. electrons (dose per pulse normalized to ~5000 rads). The dashed lines are previously determined spectra of radical ions (arbitrary scales)[12-15]: ordinate, optical density; abscissa, wave length (Å.).

(*d*) *Nitrobenzene.* The presence of a transient band at 4600 Å. is consistent with the observation of a peak at the same wave length on γ irradiation of nitroben- zene in methyltetrahydrofuran.[6] The similarity in the rates of decay of the two transient peaks at 4600 and 3700 Å. might be taken to mean that the two peaks
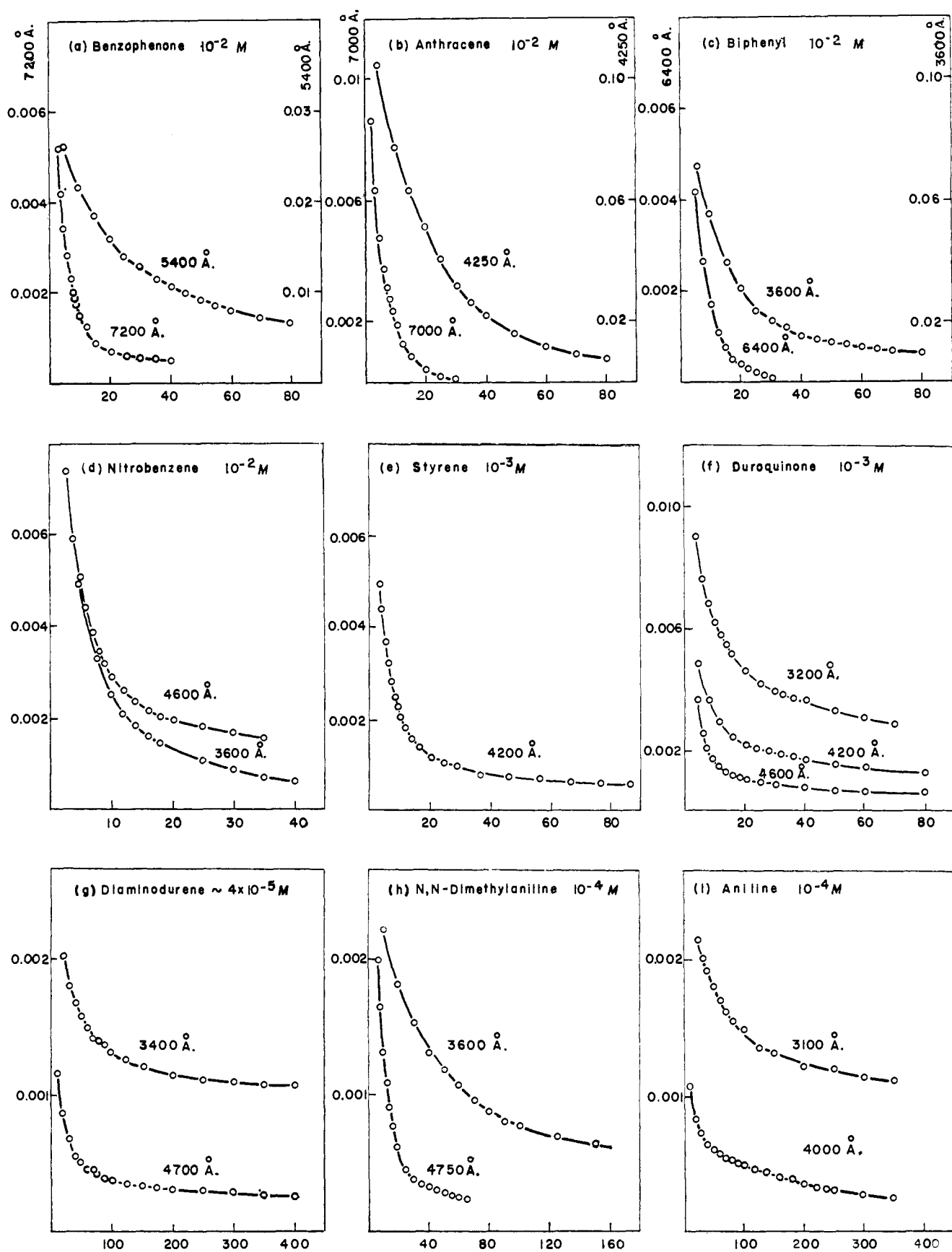
Figure 2. Optical density *vs.* time curves for the various transient absorption spectra observed (dose ~5000 rads): ordinate, optical density; abscissa, time (μsec.).

are due to the same species. The absorption maxima of the nitrobenzene radical anion (sodium salt) in dimethylformamide have been reported[19] as lying at

4650 Å. (ϵ 1200 M^{-1} cm.$^{-1}$) and 4350 Å. (ϵ 1450 M^{-1} cm.$^{-1}$). No peak in the region of 3700 Å. was ob-

(19) W. Kemula and R. Sioda, *Nature*, 197, 588 (1963).

served for this species. For this reason it seems likely that on pulse radiolysis *either* two different species are formed which decay at approximately the same rate (the one absorbing at 4600 Å. possibly being mainly a nitrobenzene radical ion) *or* a single species is formed which is not a nitrobenzene ion. The triplet–triplet absorption spectrum of nitrobenzene, although sought, has not been seen and for this reason is unlikely to contribute to the transient absorption. It cannot be decided from these results whether a nitrobenzene radical ion is a main, partial, or noncontributor to the absorption around 4600 Å. obtained on pulse radiolysis.

(e) *Styrene.* The observed transient spectrum with maximum at 3900 Å. is reasonably consistent with the spectrum previously assigned to the styrene radical anion observed[6] on γ irradiation of styrene in 2-methyltetrahydrofuran and alkane–alkene glasses. The species formed in the glasses exhibited a strong band at 4100 Å. (ϵ determined to be 23,000 M^{-1} cm.$^{-1}$) and a relatively weak band at 6000 Å. (ϵ determined to be 5000 M^{-1} cm.$^{-1}$). If it is assumed that the 3900-Å. transient peak observed on pulse radiolysis is also due to a styrene radical ion, and that its extinction coefficient is 23,000 as reported, then combination of this extinction coefficient with the k/ϵ value obtained in this study leads to a second-order decay constant for the radical ion of 1.7×10^{12} M^{-1} sec.$^{-1}$. This is over 200 times the maximum diffusion-controlled rate constant in cyclohexane, calculated according to the Debye equation, $k_{II,max} = 8RT/3000\eta$. Thus either the transient spectrum observed in this pulse radiolysis study is due mainly to some other species besides a styrene radical ion (for example, an ethylene-substituted cyclohexadienyl) or it is in fact due to a styrene radical ion, and the reported extinction coefficients for the anion are too high. In view of the fact that e.s.r. studies[20] have shown that a substituted cyclohexadienyl is formed on irradiation of polystyrene, it is considered that the first possibility is the more likely; *i.e.*, some other species besides a styrene radical ion is the main cause of the 3900-Å. transient absorption.

(f) *Duroquinone.* The peaks of the neutral durosemiquinone radical and the durosemiquinone radical anion occur at approximately 4100 and 3200 Å., and 4350 Å., respectively, in liquid paraffin solution.[21] Duroquinone T–T absorption in liquid paraffin has peaks at 4600 and 4900 Å.[21] There is considerable overlap of the absorptions of these different species in the range 4000–5000 Å. However, the similarity in the decay curves at 3200 and 4200 Å. suggests that the observed absorption at these two wave lengths is due mainly to the same species, the neutral durosemiquinone radical. The faster decaying absorption at 4600 Å. may be associated with one or more of several possible species: (1) a duroquinone radical ion, (2) the duroquinone triplet state, and (3) a biradical formed from duroquinone by internal abstraction of a hydrogen atom by a carbonyl oxygen atom.[22] From the experimental data presented, it is not possible to distinguish between these various possibilities.

(g) *Diaminodurene.* The radical cation derived from diaminodurene has absorption peaks at 4800 Å.

(20) H. Fischer, *Kolloid-Z.*, 180, 64 (1962).
(21) N. K. Bridge and G. Porter, *Proc. Roy. Soc.* (London), A244, 259 (1958).
(22) N. C. Young and C. Rivas, *J. Am. Chem. Soc.*, 83, 2213 (1961).

(ϵ 9300 M^{-1} cm.$^{-1}$) and 4450 Å. (ϵ 7500 M^{-1} cm.$^{-1}$) in aqueous methanol.[23] It may be noted that in the case of amines, unlike all the solutes considered so far, the radical cation rather than the anion is the easier to prepare chemically. The 4800-Å. peak observed in the present study is likely to be due to a diaminodurene radical ion.

The longer-lived peaks at lower wave lengths are probably due to other uncharged radicals derived from diaminodurene, for example, neutral diaminodurosemiquinone.

(h) *N,N-Dimethylaniline.* The radical cation derived from N,N-dimethylaniline has a peak in the visible at 4600 Å. in aqueous solution.[15] It is therefore suggested that the peak at 4750 Å. obtained in the present study is a radical ion. Substituted cyclohexadienyl radicals may be partly responsible for the longer-lived shorter wave length peaks observed on pulse radiolysis.

(i) *Aniline.* There was little sign in the transient spectrum obtained on pulse radiolysis of a peak around 4230 Å. where the $C_6H_5NH_2^{+\cdot}$ radical cation has a maximum.[15] However, the fact that the rate of decay of absorption at 4000 Å. was much faster than at 3100 Å. proves that different species are the main cause of absorption at the two wave lengths. Thus a contribution to the absorption at 4200 Å. of a radical ion cannot be excluded. The anilino radical[15] or substituted cyclohexadienyl radicals may be the cause of the absorption around 3000 Å.

Radical Ion Yields. The yields of aromatic radical ions in these experiments were obtained by estimating the total radical ion absorption at the wave length maximum, caused by a pulse of known dose, and then calculating the ion concentration assuming an extinction coefficient for the radical ion. This could be done only when the aromatic radical ion spectra could be separated from other transient species. Extinction coefficients at the ion absorption maxima were obtained from the literature (see Table II) and were assumed for the purpose of the present calculations to be independent of solvent, physical state, and temperature. In view of the expectation that corresponding aromatic radical anions and cations would have the same spectrum, it was assumed that the extinction coefficients of anion and cation are identical. Thus the yields calculated are for the sum of anions and cations. In view of all the sources of error, including the decay of absorption during the pulse, it is estimated that the yields of ions obtained are correct to no better than ±50%.

The yields obtained for the different solutes at various concentrations are given in Table II. The first three solutes in the table gave well-defined ion absorption maxima resulting in yields up to 0.6 depending on solute concentration. In the case of nitrobenzene and styrene, estimates of the ion yield could not be made since transient absorptions that could be definitely identified with radical ions were not obtained. However, the results obtained are quite consistent with ion yields up to $G = 0.6$. For duroquinone an upper limit for ion production was obtained by assuming all the transient absorption at 4300 Å. was due to radical ion. The yield in the case of diaminodurene is low, probably

(23) L. Michaelis, M. P. Schubert, and S. Granick, *ibid.*, 61, 1981 (1939).

Table II. Radical Ion Yields

Solute	Solute concn., M	Lit. data for radical ions			G value for radical ions
		Absorption max., Å.	ϵ, M^{-1} cm.$^{-1}$	Ref.	
Benzophenone	10^{-4}–10^{-1}	6300	5,000	a	0.15–0.48 (see Figure 3)
Anthracene	3×10^{-6}–10^{-2}	7150	9,240	13	0.08–0.32 (see Figure 3)
Biphenyl	10^{-2}	6400	11,700	14	0.42
	10^{-1}				$\sim$0.6
Nitrobenzene	10^{-2}	4350	1,460	19	See text
Styrene	10^{-3}	4100	23,000	6	See text
Duroquinone	10^{-3}	4300	7,400	b	$\leqslant$0.2
Diaminodurene	$\sim$4 $\times$ 10^{-5}	4800	9,300	23	0.08
N,N-Dimethylaniline	10^{-4}	4600	2,000	c	$\sim$0.3
Aniline	10^{-4}	4230	2,000	c	$\leqslant$0.04
Iodine^e	10^{-4}	3800	15,600	d	$\leqslant$0.2
	3×10^{-3}				$\sim$0.4
	10^{-2}				$\sim$0.5

^{a} A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963). ^{b} H. Diebler, M. Eigen, and P. Matthies, *Z. Elektrochem.*, **65**, 634 (1961). ^{c} E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963). ^{d} L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957). ^{e} See ref. 10.

because of the low solute concentration used (this solute is not very soluble in cyclohexane). For N,N-dimethylaniline and aniline the estimated yields are very approximate owing to uncertainty in extinction coefficient. Also in the case of aniline, a clear maximum at the reported ion absorption peak was not obtained, so that only an upper limit of yield could be estimated.

In the cases of benzophenone and anthracene, the radical ion yields were measured as a function of solute concentration. The variations of yield with concentration, calculated from the results given in Tables I and II, are shown in Figure 3. The reduction in yield at low solute concentration may be due to the failure of the solute to scavenge all ions, and the possible increase at high solute concentrations may be due to direct effects, interference with molecular yields, etc. The constant portion of the curve represents the state when all scavengeable ions formed in the solvent are captured by the solute.

The results obtained with all the different solutes used conform with the general picture that at solute concentrations of up to 10^{-1} M yields of radical ions lie between 0 and 0.6. Furthermore, the ion yield is probably constant over a wide range of solute concentration, the actual range depending on the nature of the solute. The yields obtained were of the same order of magnitude as found by Allen and Hummel,[2] Freeman,[3] and Williams[24] for low-dose-rate irradiation of various aliphatic hydrocarbons. However, the yields are almost an order of magnitude lower than the yields of scavengeable electrons implied by the results of Scholes and Simic[4] for low-dose-rate γ irradiation of cyclohexane in the presence of nitrous oxide.

The difference can be explained if we suppose that the electrons are formed on radiolysis of aliphatic hydrocarbon liquids with a range of energies; some of them escape the immediate region of the corresponding positive ion ($G \sim$ 0.2–0.3) and some of them do not escape ($G \sim$ 2–3). It may be that all the electrons react with each of the scavengers under consideration, at suitable scavenger concentrations. In the case of the aro-

(24) F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).

matic scavengers, such of the radical anions as are formed from electrons which have not escaped the immediate region of the positive ion ($G \sim$ 2–3) may recombine with positive ions, so that only those anions formed from electrons which have escaped can be detected. In the case of N_2O, however, electron capture by N_2O may lead to decomposition to N_2 and O_2^- before charge neutralization. Alternatively, N_2O^- may be formed and may decompose during the neutralization process. Thus the N_2O system may permit a measurement of the total electron yield instead of only the yields of ions which escape rapid ion-pair recombination.
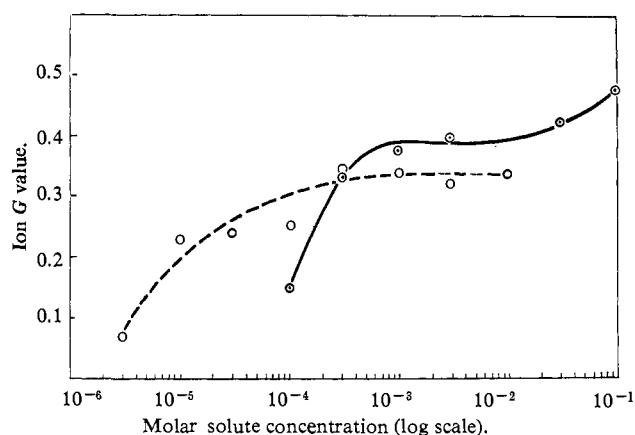

Figure 3. Effect of solute concentration on the yields of radical ions: —⊙—, benzophenone; ---O---, anthracene.

The yields of between $G = 1$ and 2 for aromatic radical ions trapped in hydrocarbon glasses at liquid nitrogen temperature observed by Ronayne, Guarino, and Hamill,[5] are understandable in these terms. It is possible that the yields of excited states of the various scavengers that have been used are closely connected with the ion yields obtained. The excited reactants formed by rapid ion recombination may give rise to the T–T absorptions observed for some solutions.

With 10^{-1} M biphenyl and 10^{-2} M anthracene, an attempt was made to find evidence for a further yield of very rapidly decaying ions, with lifetimes of the order

of tenths of a microsecond, by examining absorption changes during the 2-μsec. pulse. An indication was found of 10–20% more ions under these conditions. This appears to be consistent with the model of Free-

man and Fayadh.[25] Any yield of ions with still shorter lifetimes could only be observed using pulses with durations in the nanosecond range.

(25) G. R. Freeman and J. H. Fayadh, *J. Chem. Phys.*, 43, 86 (1965).

Photoinitiation of Unimolecular Reactions.
The Photolysis of 2,3-Diazabicyclo[2.2.1]hept-2-ene

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The gas-phase photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (I) with 337-mμ light has been investigated in the pressure range 10–1000 μ. The variation in the yields of hydrocarbon products, bicyclo[2.1.0]pentane (II), cyclopentene (III), and 1,3-cyclopentadiene (IV), with pressure is consistent with the initial formation of "hot" II which can either be deactivated or isomerize to "hot" III. The latter can either undergo unimolecular decomposition to yield IV or be deactivated. Changing the wave length of irradiation from 313 to 334 mμ changed the relative yields of the products in a manner consistent with this "hot" molecule mechanism.

Introduction

It has been recognized for some time that unimolecular reactions which have been photoinitiated should provide more specific information for energy transfer and rate studies than the corresponding thermal systems. Preliminary work[1] indicated that the photodecomposition of cyclic azo compounds such as 2,3-diazabicyclo[2.2.1]hept-2-ene (I) might prove to be a convenient source of vibrationally excited strained ring hydrocarbons which would undergo unimolecular reaction. These systems have the advantage that the nitrogen produced acts as a monitor of the hydrocarbons formed so that the over-all stoichiometry can be checked. Also the unimolecular reactions of the hydrocarbons formed have been studied in conventional thermal systems.[2–4]

Experimental Section

Procedure. The azo compound I, whose preparation has been previously described,[5] was vaporized into the reaction vessel and the pressure measured by means of both a quartz spiral gauge (Texas Instruments) and, where applicable, by a Pirani gauge which had been calibrated for I. The pressure range covered was limited by the vapor pressure of I at room temperature, *viz.*, 2.5 mm.

(1) C. Steel, *J. Phys. Chem.*, 67, 1779 (1963).
(2) M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, 84, 2688 (1962).
(3) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, 86, 679 (1964).
(4) D. W. Vanas and W. D. Walters, *ibid.*, 70, 4035 (1948).
(5) S. G. Cohen, R. Zand, and C. Steel, *ibid.*, 83, 2895 (1961).

Most photolyses were carried out to completion in a reactor at 44° equipped with 16 "black light" lamps (General Electric F8-T5-BLB). A 500-mm. grating monochromator (Bausch and Lomb) and a high-pressure mercury arc (PEK 110) were used for the experiments requiring monochromatic light.

All absorption spectra were obtained on a Cary 14 spectrophotometer, while a Zeiss spectrofluorometer was used for obtaining fluorescence spectra.

Analyses for bicyclo[2.1.0]pentane (II), cyclopentene (III), and 1,3-cyclopentadiene (IV) were effected by a flame ionization gas chromatograph equipped with a 25-ft. glass column packed with 10% SF-96 on Chromsorb W 60/80. We originally employed a silver nitrate column as in our earlier work, since this is a common column for the separation of olefins,[6] but we found that the fraction of injected IV which passed through this column depended drastically on both the size of the sample and the past history of the column. This is probably the reason why we did not originally observe this compound since the early studies,[1] with the exception of two runs, were carried out at pressures above 1 mm. where we now know IV is only a minor product. The identities of the compounds II, III, and IV were confirmed by mass spectral analyses. A small amount of 1,4-pentadiene ($\leqslant 2\%$), as identified by gas chromatography, was also formed. Total hydrogen and nitrogen were estimated by conventional gas analyses employing a gas buret and Toepler pump. The relative amounts of the two gases were determined by gas chromatography using a molecular sieve column and a thermal conductivity detector. Good agreement between the yields of H_2 and IV was obtained. Thus at 35 μ and for a 2-l. reaction vessel we found $H_2/N_2 = 0.379$ and $IV/(II + III + IV) = 0.396$.

Absorption on Glass. It was established that in the pressure range accessible for study, *viz.*, 10–1000 μ, the azo compound I was strongly adsorbed on Pyrex glass surfaces. This was first observed by noting that the hydrocarbon product ratios were sensitive to the surface to volume ratio of the photolysis vessel employed when the latter was changed from a 2-l. bulb to a coiled length of 6-mm. tubing. The effect was confirmed by measurement of the fraction of I absorbed. To do this a given pressure of azo compound, as read

(6) B. Smith and R. Ohlson, *Acta Chem. Scand.*, 13, 1253 (1959).