

TABLE VIII
PRODUCTION OF BROMOCHLOROBENZENES

(RN ₂ R) ₀ , mole l. ⁻¹	(Br ₂) ₀ , mole l. ⁻¹	Yield, % ^a
		Bromochlorobenzenes
...	1.44	10
0.100	1.35	27
...	2.66	16
0.100	2.70	40

^a Based on bromine.

RN₂R were heated in sealed ampoules for 8 days at 80.0°. Aliquots from the reaction mixtures were subjected to vapor phase chromatography on a silicone column at 172°. Symmetrical peaks were obtained at the retention time characteristic

of *p*-bromochlorobenzene. Aliquots from samples of the reaction mixtures in which bromine had been destroyed with acetone showed identical peak areas. No peaks characteristic of *m*- and *o*-bromochlorobenzene were observed since their retention times under these conditions were almost identical with the retention time for the *para*-compound. Yields were determined by comparison of the peak areas with those obtained from chromatograms of solutions containing known amounts of *p*-bromochlorobenzene. The results are shown in Table VIII.

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Cage Effects in Thermal and Photochemical Decomposition of an Azo Compound

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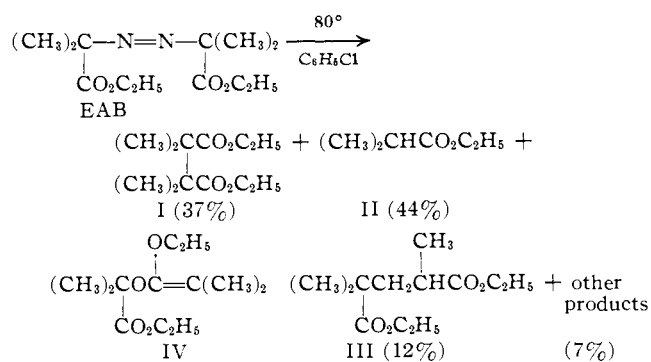
Ethyl 2,2'-azobisisobutyrate has been decomposed both thermally and photochemically. In the presence of low concentrations of radical scavengers both reactions are measurably inefficient in the production of kinetically free radicals. Small differences in the efficiency factors are attributed to differences in the temperatures of the two kinds of experiments and we conclude that the fundamental processes in thermolysis and photolysis are essentially identical.

Thermal decomposition of azonitriles¹ and azoamides² is measurably inefficient in the production of radicals that become available for reaction with small concentrations of scavengers and for the initiation of chain reactions such as vinyl polymerization³ and hydrocarbon oxidation.⁴ The inefficiency has usually been attributed to geminate recombination of radical pairs, although nonradical mechanisms for thermal decomposition can be formulated. Evidence against the radical mechanism of the inefficient reaction was presented by Roy, Nash, Williams, and Hamill⁵ who studied iodine scavenging in both the thermal and photochemical decomposition of azobisisobutyronitrile (ABN). They found that variation of the iodine concentration up to 0.1 *M* did not increase the amount of iodine incorporated into organic reaction products whereas iodine incorporation in photochemical experiments increased monotonously as the iodine concentration was raised from 10⁻³ to 0.3 *M*. Variation in the latter case was attributed to competition by the scavenger with secondary recombination of geminate radicals; consequently they also concluded that there was no geminate recombination in the thermal reaction. We have presented evidence that in the thermal decomposition of another azonitrile, iodine scavenging, attributed to reaction with geminate radical pairs, only becomes important at scavenger concentrations above 0.1 *M*⁶ and it has been pointed out^{1,6} that alternative explanations of the photochemical results are possible. However, further detailed comparison of the efficiencies

of radical production by thermal and photochemical decomposition of the same compound seems to be of considerable interest. Since decomposition of azonitriles by either photochemical⁷ or thermal reactions is complicated by intermediate formation of unstable ketenimines, we chose to make the comparison using an azo ester, ethyl 2,2'-azobisisobutyrate (EAB).

Results and Discussion

Thermal decomposition of EAB in chlorobenzene solution and in the absence of oxygen gives products as indicated in the equation. The structure of a possible isomeric coupling product (IV) is also shown.



The results are comparable to those reported for the corresponding methyl ester by Bickel and Waters⁸ except that they reported a 4% yield of methyl methacrylate. We find that no detectable amount of ethyl methacrylate is formed. The apparent minor discrepancy is probably not real since Bickel and Waters estimated the product by catalytic hydrogenation of a solution containing all the reaction products. The 7% products of unknown structure may include some un-

(1) G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *J. Am. Chem. Soc.*, **82**, 5394 (1960), and references cited therein.

(2) G. S. Hammond and R. C. Neuman, Jr., *ibid.*, **85**, 1501 (1963).

(3) L. M. Arnett, *ibid.*, **74**, 2027 (1952); L. M. Arnett and J. H. Peterson, *ibid.*, **74**, 2031 (1952).

(4) G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

(5) J. C. Roy, J. R. Nash, R. R. Williams, and W. H. Hamill, *ibid.*, **78**, 519 (1956).

(6) H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964).

(7) P. Smlth and A. M. Rosenberg, *ibid.*, **81**, 2037 (1959).

(8) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 312 (1950).

saturated materials. Ethyl methacrylate is undoubtedly formed by disproportionation but is apparently consumed by addition of radicals. Disproportionation of the adduct radical is an obvious source of ethyl α, α, α' -trimethylglutarate (III). The results are similar to those obtained with azonitriles except that relatively less coupling, to form ethyl tetramethylsuccinate (I), occurs. Evidence for formation of an isomeric coupling product, such as the ketenacetal IV, was sought in both thermal and photochemical reactions, but the results were entirely negative.

Thermal decomposition of EAB in chlorobenzene and in the absence of oxygen follows very clean first-order kinetics. The results are summarized in Table I. Calculated values of the energy and entropy of activation at 81.3° are, respectively, 29.4 kcal. per mole and 4.8 cal. per mole per degree. The parameters are rather similar to those involved in 1,1'-azocyanocyclohexane (ACC) decomposition.⁹

TABLE I
RATE CONSTANTS FOR THE THERMAL DECOMPOSITION OF EAB IN CHLOROBENZENE

T, °C.	[EAB] ₀ , mole l. ⁻¹	10 ³ k, min. ⁻¹
92.6	0.15	3.585
92.6	.05	3.577
92.6	.15 and 0.05	3.580 ± 0.007 ^a
70.0	.05	0.2490 ± 0.0009 ^a

^a Errors quoted are standard errors of the final mean rate constants.

The efficiency of radical production at 70° was measured by the oxidation-inhibition method⁴ using both 2,6-di-*t*-butyl-*p*-cresol (DBPC) and N,N'-diphenyl-*p*-phenylenediamine (DPPD) as inhibitors. Results are shown in Table II along with results obtained earlier for ABN and ACC.

TABLE II
THE OXIDATION OF CUMENE IN CHLOROBENZENE, INITIATED BY EAB AND INHIBITED BY DBPC AND DPPD, AT 70° AND 1 ATM. O₂ PRESSURE

10 ² [EAB] ₀ , moles l. ⁻¹	10 ² [DBPC], mole l. ⁻¹	10 ² [DPPD], mole l. ⁻¹	Inhibition period, min.	Eff.iciency, ^{a,b}	-dO ₂ /dt, ml. min. ⁻¹
6.098	0.1352
9.211	0.1682
15.82	0.8885	40.6	0.63
11.48	0.7137	42.9	0.66

^a Rate constant for N₂ evolution from EAB decomposition in 2:1 chlorobenzene-cumene at 70° was (2.296 ± 0.014) × 10⁻³ min.⁻¹ ^b Corresponding values for ABN and ACC are 0.62¹³ (at 70°) and 0.60⁹ (at 79.7°), respectively.

Solutions of EAB were irradiated in benzene and carbon tetrachloride using 3660 Å. light isolated from the emission of a high pressure mercury arc with suitable filters. Decomposition of EAB was followed spectrophotometrically and light intensities were monitored using the ferrioxalate actinometer.^{10,11} Quantum yields

(9) C.-H. S. Wu, G. S. Hammond, and J. M. Wright, *J. Am. Chem. Soc.*, **82**, 5386 (1960).

(10) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

(11) Lee and Sellger have reported at the Rochester Photochemistry Symposium, March, 1963, that the quantum yield of the ferrioxalate actinometer is higher than reported by Hatchard and Parker. Since Hatchard and Parker, and also Baxendale and Bridge,¹² have correlated data for ferrioxalate with those for uranyl oxalate, we tentatively accept the lower value. Since results reported in this paper are only used in a relative sense, the present conclusions would not be affected by a change in the value.

(12) J. H. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955).

for destruction of the azo compound were close to 0.416 in benzene and 0.408 in carbon tetrachloride with the difference between the two values lying just outside of the probable experimental error. The results were independent of the extent of reaction; the quantum efficiency is very close to the value of 0.47 for the photolysis of ABN in benzene.⁷ A complete product analysis has not been carried out, but infrared examination of solutions immediately after irradiation and after a period of heating following irradiation indicated that no metastable product, such as IV, was produced. Data are shown in Table III.

TABLE III
QUANTUM YIELDS FOR THE PHOTOCHEMICAL DECOMPOSITION OF EAB (Φ_{EAB}) AT 25°

Solvent	[EAB] ₀ , mole l. ⁻¹	10 ⁻¹⁶ I, qu. sec. ⁻¹	10 ⁴ t, sec. ^b	% decompn.	Φ_{EAB} ^a
Benzene	0.1207	2.57	16.0	5.6	0.408
Benzene	.1207	2.56	24.0	8.5	.415
Benzene	.1207	2.56	24.0	8.8	.429
Benzene	.1197	2.35	21.0	7.1	.428
Benzene	.1197	2.12	77.5	22.8	.412
Benzene	.1197	2.03	105.05	29.5	.411
Benzene	.1197	1.81	161.3	40.9	.416
Carbon tetrachloride	.1196	3.23	63.0	28.0	.409
Carbon tetrachloride	.1196	3.10	63.0	26.8	.408
Carbon tetrachloride	.1196	2.95	77.2	31.2	.406
Carbon tetrachloride	.1196	2.68	77.2	28.5	.409

^a Mean values are 0.416 ± 0.003 in benzene and 0.408 ± 0.001 in carbon tetrachloride; errors are standard errors. ^b 4.126-ml. samples were irradiated; *t* and *I* signify time of irradiation and mean intensity, respectively.

Solutions of EAB and iodine in carbon tetrachloride were irradiated with the 3660 Å. band and the rates of iodine consumption were measured. Disappearance of iodine followed zero-order kinetics and iodine lifetimes were estimated by extrapolation. Quantum yields, shown in Table IV, were found to be independent of initial concentrations of both iodine and EAB. The value of Φ_{I_2}/Φ_{EAB} , the efficiency factor for radical production in the photolytic reaction, is 0.38. The reactions in the presence of iodine involved only low conversion of EAB (~3%) during the intervals required to consume all of the iodine. However, an approximate value of Φ_{EAB} of ~0.5 was measured for runs with iodine present. The result is in satisfactory agreement with values measured at higher conversions in the absence of iodine.

TABLE IV
IODINE LIFETIMES (*t*₁) AND QUANTUM YIELDS FOR IODINE CONSUMPTION (Φ_{I_2}) AT 25°^b

[EAB] ₀ , mole l. ⁻¹	10 ¹⁶ [I ₂] ₀ , moles l. ⁻¹	10 ⁻¹⁶ I, qu. sec. ⁻¹	<i>t</i> ₁ , sec.	Φ_{I_2} ^a
0.1348	9.947	3.29	4820	0.156
.1201	7.460	3.20	3715	.156
.1207	7.460	3.38	3540	.155

^a Mean value is 0.156. ^b 4.126-ml. samples were irradiated.

Significance of the Results.—The first two values in Table V show that there is precedent for solvent effects on *a* factors in the thermal decomposition of ABN and that *a* is greater in chlorobenzene than in carbon tetrachloride at the same temperature. The second pair of figures show that there is virtually no difference between the *a* factors for ABN and EAB under identical conditions. Thus it would seem likely

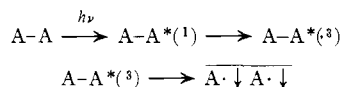
that a for the thermal decomposition of EAB in carbon tetrachloride at 62.5° is close to 0.45 and similar to the value for the photolysis of this compound at 25° (0.38). It would not be surprising if this small difference turned out to be genuine since it would be reasonable to expect that diffusion of geminate radicals from the cage be enhanced as the temperature is raised due, for example, to a decrease in solvent viscosity.

TABLE V
EFFICIENCY FACTORS (a) FOR THE THERMAL DECOMPOSITION OF AZO COMPOUNDS

Azo compd.	Solvent	T , °C.	a
ABN	Chlorobenzene ⁴	62.5	0.59
ABN	Carbon tetrachloride ⁴	62.5	.45
ABN	Chlorobenzene ¹³	70	.62
EAB	Chlorobenzene	70	.64

The results seem fairly conclusive in showing that thermolysis and photolysis become essentially identical decomposition processes by the time separation of geminate radicals can occur. Any excess energy associated with fragments from photolysis must be lost in relaxation processes that are fast compared to dissociation.

An interesting possibility in photolyses is that intersystem crossing to a triplet state might precede dissociation. In that event the radical pair should be produced with parallel electron spins and the amount of geminate recombination *might* be reduced.



The present evidence indicates that in the photolysis of EAB one of two circumstances obtains: either (1) decomposition occurs from the excited singlet state or (2) spin transitions of the radical pair are fast in comparison with diffusive movements.

Our results contrast with those reported for ABN.⁵ Although different substrates were used in the two studies, our results indicate that some reservation concerning the exact significance of the role of iodine in photodecomposition of the azonitrile is in order.

Study of the photolysis of EAB, especially in the presence of photosensitizers, is being continued.

Experimental

Solvents.—**Chlorobenzene** (Matheson Coleman and Bell reagent grade) was purified as described in the accompanying paper⁶ except that the procedure for removal of last traces of scavenger was omitted. **Cumene** (Matheson Coleman and Bell reagent grade) was purified by repeated extraction with concentrated sulfuric acid until both layers were colorless, washing (water, saturated sodium bicarbonate solution, water), drying (magnesium sulfate and Drierite), and fractional distillation under nitrogen. The middle fraction was collected and stored in a refrigerator. **Benzene** (Baker Chemical Co., analyzed reagent grade, thiophene-free) was dried with sodium and fractionated through a Vigreux column. The middle fraction was used in these experiments. **Carbon tetrachloride** (Mallinckrodt reagent grade) was dried (calcium chloride) and distilled before use.

Other Commercial Materials.—**2,6-Di-*t*-butyl-*p*-cresol** (Eastman Kodak Yellow Label) was purified by recrystallization from ethanol; m.p. 70°. ***N,N'*-Diphenyl-*p*-phenylenediamine** (K and K Laboratories) was recrystallized from chlorobenzene; m.p. 144°. **Iodine** (Baker and Adamson reagent grade) was used without further purification.

Ethyl 2,2'-azobisisobutyrate (EAB) was prepared from 2,2'-hydrazoisobutyronitrile which was made in the manner described

by Thiele and Heuser.¹⁴ The hydrazonitrile was hydrolyzed following their procedure and esterified by the method of Bickel and Waters⁸ using ethanol instead of methanol. The crude hydrazo ester was distilled at reduced pressure using a short Vigreux column (b.p. 76–78° (0.08 mm.)) and further purified by preparative vapor phase chromatography with a 6-ft. Carbowax column at 183°. This material was distilled twice at reduced pressure through a Vigreux column (b.p. 229–230° (745 mm.)).

*Anal.*¹⁵ Calcd. for C₁₂H₂₄N₂O₄: C, 55.36; H, 9.29; N, 10.76. Found: C, 55.46; H, 9.30; N, 10.72.

The pure hydrazo ester was oxidized by the method described¹⁴ and the crude product recrystallized several times from purified ligroin (30–60°) using acetone and solid carbon dioxide for a coolant. The ligroin solution of EAB was dried and evaporated at reduced pressure and room temperature to yield a pale yellow liquid.

Anal. Calcd. for C₁₂H₂₂N₂O₄: C, 55.79; H, 8.59; N, 10.85. Found: C, 55.90; H, 8.61; N, 10.60.

The n.m.r. spectrum of the purified EAB in carbon tetrachloride was very clean and compatible with the structure of the compound. It also showed the absence of hydrazo ester. A sample decomposed in chlorobenzene at 70° gave 100.3% of theoretical nitrogen. The ultraviolet spectrum of EAB in cyclohexane (Table VI) was compared with that obtained from a gift sample (E. I. du Pont de Nemours and Co.) after rigorous purification by low temperature crystallization. The two spectra were identical. Comparison of extinction coefficients was used thereafter as a criterion of purity.

TABLE VI
THE ABSORPTION SPECTRUM OF EAB IN CYCLOHEXANE

λ , m μ	ϵ^a	λ , m μ	ϵ	λ , m μ	ϵ
380	16.3	350	17.8	230	648
370	20.2	280	0.0	220	1024
363 (max)	20.9	250	45.8	210	1405
360	20.5	240	258		

^a Molar extinction coefficient.

Synthesis of Reaction Products.—**Ethyl tetramethylsuccinate (I)** was prepared from tetramethylsuccinic anhydride obtained from Dr. Neuman.² Tetramethylsuccinic acid was obtained by hydrolysis of the anhydride in the presence of excess sodium hydroxide. The crude acid obtained on acidification of the alkaline solution was purified by way of the potassium salt. The silver salt of tetramethylsuccinic acid was made from its ammonium salt. The dry silver salt was suspended in dry benzene and a 100% excess of fractionated ethyl iodide added slowly. After refluxing for 12 hr., the solution was cooled, and the precipitated silver iodide was filtered and washed with ethanol, and the washings were poured into water. The benzene mother liquor was combined with a benzene extract of this aqueous solution, washed, and dried. The solvent and excess ethyl iodide were removed by evaporation at reduced pressure and the residue distilled through a Vigreux column. The fraction boiling at 54.8–55° (0.08 mm.) was collected. It had b.p. 219.5° (745 mm.). Analytical vapor phase chromatography showed the absence of trace impurities.

Ethyl isobutyrate (II).—Isobutyric acid (Matheson Coleman and Bell reagent grade) was esterified by refluxing it for 19 hr. in six times its volume of 10% (by volume) concentrated sulfuric acid in absolute ethanol. The cooled solution was poured into an ice-water slurry, the organic layer separated and combined with an ether extract of the aqueous layer. The ether solution was washed, dried, and filtered. Ethyl isobutyrate was obtained by fractionating the residue, after evaporation of solvent, through a Vigreux column. The fraction boiling at 109.8–110° (745 mm.) was collected. Analytical vapor phase chromatography showed the absence of trace impurities. **Ethyl methacrylate**, monomer (Matheson Coleman and Bell reagent grade), was used in the product analysis without purification.

Ethyl α,α,α' -trimethylglutarate (III) was synthesized from silver powder and ethyl α -bromoisobutyrate by the method of Auwers and Meyer.¹⁶ Auwers and Ziegler¹⁷ later confirmed the identity of III by unambiguous synthesis. α -Bromoisobutyric acid was prepared from freshly fractionated isobutyric acid by

(14) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

(15) Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(16) K. Auwers and V. Meyer, *Ber.*, **23**, 293 (1890).

(17) K. Auwers and E. Ziegler, *Ann.*, **292**, 220 (1896).

(13) G. S. Hammond and U. S. Nandi, unpublished results.

reaction with liquid bromine in the presence of a catalytic amount of phosphorus trichloride. The mixture was heated at 80° for 6 hr. and then at 100° for 2 hr. The low boiling material was evaporated at reduced pressure and the residue fractionated through a Vigreux column. It had m.p. 48° and was esterified in the same way as isobutyric acid. The fraction boiling at 160.5–161° (745 mm.) was collected.

Silver powder was made by reducing silver chloride with sodium hydroxide and dextrose in aqueous solution. It was washed (ethanol, then ether) and dried. Reaction with ethyl α -bromoisobutyrate was effected in the manner described.¹⁶ That portion of the reaction product boiling at 100–120° (0.05 mm.) was collected and subjected to vapor phase chromatography (12-ft. Apiezon J column at 195°). By comparison of retention times, one of the two expected major products¹⁶ was shown to be ethyl tetramethylsuccinate (I). A portion of the other major product¹⁶ (III) was collected.

Product Analysis.—A chlorobenzene solution, 0.5 *M* in EAB, was degassed, sealed *in vacuo*, and immersed in an oil bath at 80° for 900 min. This corresponds to eleven calculated (Table I) half-lives at this temperature. The flask was cooled and opened and the products identified by comparison of retention times with authentic samples on a 12-ft. Apiezon J column at 195°. Quantitative analysis of the mixture was effected by comparison of the peak areas with those from chromatograms obtained from synthetic mixtures of approximately the same composition.

Rates of Nitrogen Evolution.—Rates of nitrogen evolution in the thermal decomposition of EAB (Table I) were monitored manometrically by the method described.² All kinetic runs were effected in duplicate or triplicate; determinations of nitrogen evolved were made about 15 times in each run. First and last readings were taken at *ca.* 15 and 70% reaction, respectively. Rate coefficients, *k*, were obtained from the integrated form of the first-order rate equation and were constant, within the limits of experimental error, for any one run.

Measurement of Efficiency Factors.—Efficiency measurement in the thermal decomposition of EAB (Table II) was made by the method of oxidation inhibition.⁴ Oxidation rates were measured with the same apparatus used for the study of rates of nitrogen evolution.² The inhibition periods for oxidation of cumene (33% by volume) in chlorobenzene initiated by EAB and inhibited by DBPC and DPPD were very clearly defined. Efficiency factors were calculated as described.²

Photolytic Reactions.—**Apparatus:** All photolyses described in this paper were effected with light isolated from a Westinghouse (SAH 800-c) 800-w. short arc, medium pressure, mercury lamp, housed in the apparatus described,¹⁸ with Corning filters No. 0–52 and 7–37 in series. The transmission of the system at 3660 Å. was 17%, that at 3910 Å. was 0.05%, and that at 3340 Å. was about 0.006%. In these experiments, all the transmitted light was absorbed by the reactants. **Reaction Vessels and Degassing Procedure:** Scrupulously clean (detergent washed), matched, cylindrical Pyrex tubes (15 mm. external diameter) were employed as reaction vessels for all photolyses. Constant volumes (4.126 ml.) of reactants were placed in the tubes with a spring-loaded syringe and degassed (3 freeze–thaw cycles at 10^{–4} mm.) by attaching to a vacuum system (standard taper joint).

(18) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

A small trap at the top of each tube prevented vacuum grease from entering the tubes. **Actinometry:** The potassium ferrioxalate system was employed.¹⁰ The quantum yield for ferrous ion production at 25° and 3660 Å. was taken¹⁰ as 1.21. Light intensities were monitored just before, during, and after sample irradiation by exposure of constant volumes of ferrioxalate solution contained in tubes identical with those in which EAB decomposition was carried out. It was found that intensity decreased linearly with time. Mean intensities for the period of sample irradiation were employed in the calculation of quantum yields.

Measurement of Quantum Yields.—**Quantum Yields for EAB Decomposition** (Table III): Sufficient EAB to make the solution *ca.* 0.1 *M* in this substrate when diluted to the mark with benzene or carbon tetrachloride was weighed into a volumetric flask. Samples were prepared as described above and shaken periodically during irradiation. At convenient time intervals, tubes were opened, 2-ml. samples diluted to 5 ml. with the appropriate solvent, and optical densities of 1 cm. solutions measured at 100–Å. intervals over the range 3300 to 4000 Å. together with a similarly treated sample that had not been irradiated. Pure solvent was placed in the reference beam. A Beckman DU spectrophotometer was employed. Beer's law was obeyed in both solvents over and beyond the present concentration range. In any one experiment, all measurements were made at the same slit width and wave length. Thus direct comparison of optical densities indicated the amount of EAB decomposed. **Quantum Yields for Iodine Consumption** (Table IV): Samples were prepared by dilution of weighed quantities of EAB (freshly prepared) and iodine to known volume. The presence of iodine did not affect the absorption of EAB in carbon tetrachloride. The rate of disappearance of iodine in each tube was measured spectrophotometrically at 5150 Å. (Beer's law was obeyed over and beyond the present concentration range) by repeated direct measurement of optical densities after successive periods of irradiation. A tube containing solvent was placed in the reference beam. Wave length and slit width were unaltered during an experiment. Iodine lifetimes were estimated by extrapolation to zero optical density.⁴ The results of a typical experiment are shown in Table VII where the extrapolated iodine lifetime was 4820 sec. and the mean intensity was 3.288×10^{15} qu. sec.^{–1}.

TABLE VII

THE DISAPPEARANCE OF IODINE ON IRRADIATION OF EAB (0.1348 *M*) IN A CARBON TETRACHLORIDE SOLUTION CONTAINING IODINE (9.947×10^{-4} *M*)

Irradla- tion time, sec.	Optical density at 5150 Å.	$10^{15} I$, qu. sec. ^{–1}	Irradla- tion time, sec.	Optical density at 5150 Å.	$10^{15} I$, qu. sec. ^{–1}
0	1.142	3.335 ^a	3900	0.214	
600	0.995		4200	.145	
1800	.714		4500	.080	
2400	.572		5400	.000	3.240 ^a
3300	.353				

^a Determined graphically from the results of several actinometry determinations made during the run.

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