Photochemical Studies in Rigid Matrices. II.[1] A Study of the Photochemical Reactivity of Anthracene in Polystyrene and the Development of an *o*-Nitrobenzaldehyde Actinometer in Poly(methyl methacrylate)

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Abstract: The photochemistry of *o*-nitrobenzaldehyde and anthracene in rigid polymer films has been studied at 25° and 3340 and 3660 Å. *o*-Nitrobenzaldehyde "dispersed" in poly(methyl methacrylate), mol wt 20,000 ± 3000, undergoes the well-known photoisomerization to *o*-nitrosobenzoic acid, the quantum yield being 0.50 ± 0.06. Within experimental error, this is the same as in fluid solutions and in the pure solid. In view of the stability and convenience of this system, its use as an actinometer in the spectral region 2800–4100 Å is envisaged. Anthracene "dispersed" in polystyrene, mol wt 47,000 ± 4000, undergoes photodimerization at a rate much reduced from that in fluid solutions or in a potassium bromide pellet. The nature of the "dispersion" of the anthracene in the film differs significantly from its state in potassium bromide matrices. In the presence of oxygen, the major part of the photochemical reaction leads to the formation of the photooxide of anthracene. Kinetic and mechanistic details are discussed.

Many groups of workers in recent years have investigated the use of rigid polymers as media for studies of intermolecular energy transfer,[3] hydrocarbon triplet decay,[4] oxygen diffusion rates,[5] and phosphorescence polarization studies.[6] Although the systems anthracene–polystyrene and anthracene–poly(methyl methacrylate) have figured prominently in these studies,[4a,d] all the data relate to transient species. No data exist dealing with the nature of the photolysis products formed under various experimental conditions and their extent of formation. We report here the results of such an investigation at 3660 Å and also a study of the photolysis of *o*-nitrobenzaldehyde in poly(methyl methacrylate) at 3340 and 3660 Å. Both compounds were "dispersed" in thin films of the polymer and irradiated at 25°. These investigations are an extension of our study of the effect of molecular environment on the photochemistry of these compounds when dispersed in a potassium bromide matrix,[1,7] their photochemical behavior in fluid solutions having been well characterized.[8,9]

Experimental Section

Materials. Matheson Coleman and Bell anthracene was purified by sublimation and zone refining (20 passes through 10 zones). *o*-Nitrobenzaldehyde, supplied by Aldrich Chemical Co., was recrystallized three times from 80% aqueous ethanol. Benzene solvent was Matheson Coleman and Bell spectroscopic grade.

Preparation of Polymers. Styrene monomer was supplied by Matheson Coleman and Bell. The inhibitor was removed by three washings with 5% sodium hydroxide and three with water, and then drying with calcium chloride. The styrene was then fractionally distilled at reduced pressure and a middle cut taken, bp 48° (20 mm). The styrene was polymerized by the technique of Cowie, Worsfold, and Bywater,[10] using α-methylstyrene tetramer as the initiator. The polymer had a molecular weight of 47,000 ± 4000.

Methyl methacrylate monomer was supplied byMatheson Coleman and Bell. It was purified by the method of Shultz[11] and polymerized for 72 hr at 60° in a constant-temperature bath using 0.1% (by weight) azobisisobutyronitrile initiator. The polymer had a molecular weight of 20,000 ± 3000.

Both polymers were purified by dissolving in benzene, precipitating three times in petroleum ether to remove monomer and low-molecular weight polymer, and then freeze-drying to remove solvent.

Preparation of Polymer Films. Polymerization of the styrene monomer containing the requisite amount of anthracene, a technique used by other workers,[3a,e,4a,5c] was avoided due to complications arising from residual monomer[3e] and modification of the polymerization kinetics by the presence of anthracene in the system.[12] Instead, a film-forming technique was used, which introduced the photochemical reactants into the films after the polymerization had been completed. The technique was as follows. The requisite weight of polymer was dissolved in the minimum volume of benzene and the solution stirred for 6 hr. Anthracene or *o*-nitrobenzaldehyde was then added and the solution stirred for an additional 2 hr in the dark. The resulting solution was poured into a petri dish with an optically flat base. The benzene was then allowed to evaporate off at a controlled rate, by inverting a beaker over the petri dish in the dark, over a period of 24 hr to leave a perfectly transparent film at the bottom of the dish. The film was then placed in a vacuum oven at 45° for 24 hr and then subjected to a pressure of 10^{-5} mm at room temperature for 96 hr to remove all residual solvent. Average film thicknesses were $(8.00 \pm 0.10) \times 10^{-3}$ cm for

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(1) Part I: J. N. Pitts, Jr., J. K. S. Wan, and E. A. Schuck, *J. Am. Chem. Soc.*, **86**, 3606 (1964).

(2) Author to whom correspondence should be sent.

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polystyrene, and (2.22 ± 0.03) × 10^{-3} cm for poly(methyl methacrylate). All film handling was carried out in red light.

Apparatus. All photochemical reactions were carried out at 25° with the film suspended in the light path of a high-pressure mercury arc (PEK 100 w) equipped with one of two interference filter systems (Jenaer Glaswerk Schott and Gen), one having a maximum transmittance of 41% at 3290 Å and a half-width of 80 Å and the other 30% at 3650 Å and a half-width of 75 Å.

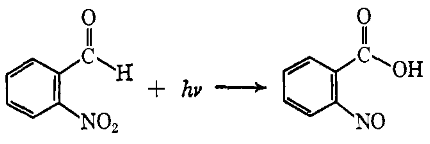
The irradiations of the anthracene films were carried out in a specially designed cell which could be evacuated to 10^{-5} mm. The cell consists of an "O-ring" seal to which two Suprasil windows are cemented and an evacuation port which can be temporarily fixed to a vacuum line. The piece of film to be irradiated is placed against one of the windows and is held in place by a piece of glass tubing extending the length of the cell. After evacuation, the cell can be filled with the appropriate atmosphere using the vacuum system and then closed and the irradiation carried out in that atmosphere. A special cradle was made for the cell to allow it to fit into the sample compartment of a Cary 15 ultraviolet spectrophotometer so that the film spectrum could be recorded as the photolysis proceeded.

Quantum-Yield Determination and Photoproduct Identification. *o*-Nitrobenzaldehyde "dispersed" in poly(methyl methacrylate) obeyed Beer's law over the entire concentration range studied. The photochemical isomerization to *o*-nitrosobenzoic acid was followed by monitoring, as a function of irradiation time, the nitro peak at 1530 cm^{-1} (asymmetrical stretching band) using a Perkin-Elmer 621 infrared spectrophotometer. Assuming a value for the quantum yield of photoisomerization to be 0.50, as obtained by careful studies in other environments,[1,9] and correcting for the fact that the film did not absorb 100% of the incident ultraviolet light, the absolute light intensity was then calculated for various irradiation times and extrapolated back to zero irradiation time. The latter extrapolation corrects absorption due to internal filtering of the ultraviolet light by the nitroso product The intensity could then be compared to that obtained using standard liquid-phase potassium ferrioxalate actinometry.[13] Direct incorporation of the potassium ferrioxalate into the polymer film was not possible because of the insolubility of the ferrioxalate in organic solvents. The nitroso product was identified by comparing the infrared spectra of a piece of film which had been subjected to prolonged irradiation and an authentic sample of *o*-nitrosobenzoic acid.

Anthracene "dispersed" in polystyrene also obeyed Beer's law over the concentration range studied Quantum yields in this system were determined from data obtained by monitoring, as a function of irradiation time, the disappearance of the anthracene absorption band at 3800 Å. Allowance was made for the fact that the anthracene absorbed only 89% of the incident light at 3650 Å even at the highest anthracene concentration studied (3.47 × 10^{-2} *M*). The incident light intensity was obtained using standard liquid-phase potassium ferrioxalate actinometry.[13] It was not possible to follow directly the rate of formation of the photolysis products because of absorption by the polystyrene in their spectral region (2200–2800 Å). All photolysis products were identified by comparison with authentic samples, prepared by the method of Bowen and Tanner,[14] using infrared analysis. Thus, all values for the quantum yields of photolysis quoted in the Results and Discussion section are quantum yields of disappearance of anthracene.

Results and Discussion

Photoisomerization of *o*-Nitrobenzaldehyde. Irradiation of *o*-nitrobenzaldehyde "dispersed" in poly(methyl methacrylate) at either 3340 or 3660 Å results in the photoisomerization of the aldehyde to *o*-nitrosobenzoic acid (eq 1) as determined by comparison of the infrared spectrum of the polymer film after photolysis with that of an authentic sample of *o*-nitrosobenzoic acid.



(1)

The results of the determination of the intensity of the light source at 3340 and at 3660 Å using *o*-nitrobenzaldehyde in poly(methyl methacrylate) film as an actinometer are shown in Table I. In view of the fact that there will be a different reflectivity associated with the film and the cell in which the potassium ferrioxalate solution was irradiated, the agreement between the intensities as determined by the two techniques is good.

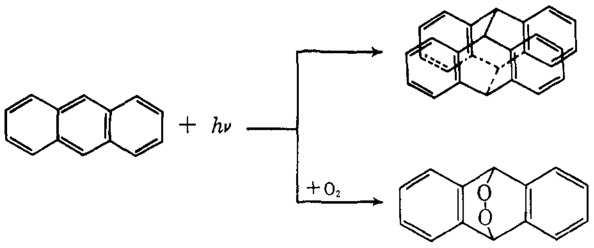
Table I. Comparison of Absolute Light Intensities, I_0, at 3340 and 3660 Å as Determined by *o*-Nitrobenzaldehyde in Poly(methyl methacrylate) Film and by the Standard Ferrioxalate Actinometer

Wave-length, Å	*o*-Nitro-benz-aldehyde, *M* (of polymer)	I_0, einsteins sec^{-1} × 10^9 A[a]	B[b]
3340	0.419	1.85 ± 0.16	1.69 ± 0.05
3340	0.823	1.80 ± 0.16	1.99 ± 0.06
3340	1.29	1.57 ± 0.15	1.76 ± 0.05
3660	0.419	3.98 ± 0.25	3.73 ± 0.10
3660	0.838	4.73 ± 0.25	4.64 ± 0.12
3660	1.31	3.37 ± 0.25	3.57 ± 0.10

[a] Incident light intensity based on assumption that ϕ isomerization of *o*-nitrobenzaldehyde = 0.50. [b] Ferrioxalate actinometer.

One can envisage that a useful actinometer could be developed using this *o*-nitrobenzaldehyde film system for photochemical studies in the range 2800–4000 Å. The film, because it is not susceptible to moisture and has better physical strength than a potassium bromide pellet, would in fact be superior to the "pellet" actinometer proposed in our earlier studies.

Photodimerization and Photooxidation of Anthracene. Irradiation of anthracene "dispersed" in polystyrene or poly(methyl methacrylate) films at 3660 Å leads to the formation of the photodimer (eq 2) and also the photooxide (eq 3) if oxygen has access to the film during the irradiation.



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(3)

In polystyrene films the photooxidation process is much more rapid than the photodimerization, in contrast to the situation where anthracene is dispersed in a potassium bromide matrix.[7] This is seen in Figure 1 which shows the change of anthracene concentration as a function of irradiation time for two identical films, one irradiated in a nitrogen atmosphere, leading to formation of the photodimer only, and the other irradiated in an oxygen atmosphere leading to the formation of the photodimer and the photooxide. Figure 1 also shows the relative rates of anthracene disappearance in two identical polystyrene films, one irradiated in a pure oxygen atmosphere and the other in air. The rates are the same in both cases. Thus, diffusion of oxygen into the film is apparently not rate controlling over the extent of reaction studied (about 20–25% conversion).

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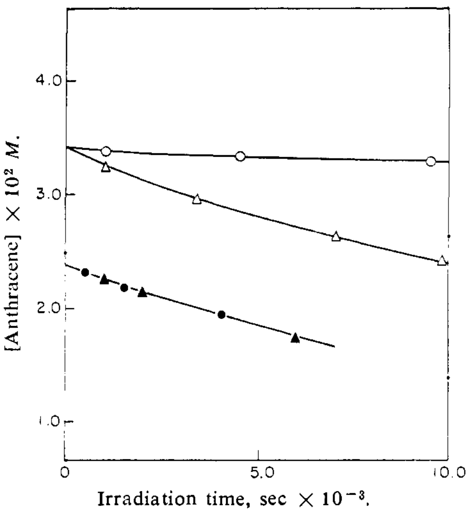

Figure 1. Effect of oxygen on the rate of disappearance of anthracene during irradiation in polystyrene at 3660 Å: ○, nitrogen atmosphere; △ and ▲, pure oxygen atmosphere; ●, air.

The quantum yields of photodimerization and photooxidation, in terms of loss of anthracene, were both strongly dependent upon the initial concentration of anthracene. This is shown in Table II where quantum yields are given for a wide range of initial anthracene concentrations at a constant film thickness [(8.00 ± 0.10) × 10^{-3} cm].

Table II. Quantum Yields[a] for the Photodimerization, Φ_{-A}, and Photooxidation, $\Phi_{-A'}$, of Anthracene in Polystyrene Film[b] at 3360 Å

$[\text{Anthracene}]_0$, $10^2 M$	$\Phi_{-A} \times 10^3$	$\Phi_{-A'} \times 10^2$
0.405		0.46
0.651	0.48	
0.660		1.00
1.13	0.68	
1.15		1.20
1.95	1.30	
2.04		2.10
2.87	1.72	
2.87		3.04
3.47	2.03	
3.40		3.46

[a] Quantum yields are in terms of loss of anthracene. [b] Film thickness (8.0 ± 0.10) × 10^{-3} cm.

Mechanism of Photodimerization. The results obtained in polystyrene film can be explained in terms of the general mechanism for anthracene photodimerization developed for fluid solutions.[14,15] This mechanism is shown in a simplified form (eq 4–8), where A,

$$\begin{array}{rcll} A + h\nu & \longrightarrow & {}^1A^* & I_a \quad (4) \\ {}^1A^* & \longrightarrow & A + \text{“energy”} & k_1 \quad (5) \\ {}^1A^* & \longrightarrow & {}^3A^* & k_2 \quad (6) \\ {}^3A^* & \longrightarrow & A + \text{“energy”} & k_3 \quad (7) \\ {}^1A^* + A & \longrightarrow & A_2 & k_4 \quad (8) \end{array}$$

${}^1A^*$, and ${}^3A^*$ are anthracene in its ground, excited-singlet, and excited-triplet states, respectively, and A_2 is the photodimer. Steps 5 and 7 include all photophysical processes by which A returns to ground state.

Making the usual steady-state approximations, the following expression can be derived for the quantum yield of photodimerization in terms of disappearance of anthracene, Φ_{-A}.

$$\Phi_{-A} = \frac{2k_4[A]}{k_1 + k_2 + k_4[A]}$$

If $k_4[A] \ll k_1 + k_2$, which seems reasonable in view of the small values for the measured quantum yields (Table II), then a plot of Φ_{-A} *vs.* [A] should be a straight line with any deviations from linearity occurring at high values of [A]. Such a plot is indeed linear at lower concentrations. At the highest [A] there is an indication of a deviation from linearity, but this falls within the limits of our experimental error and hence may not be real. The slope of the plot is 6.25 × 10^{-2} M^{-1} and thus $k_4/(k_1 + k_2) \simeq 3.13 \times 10^{-2}\ M^{-1}$.

If one assumes that reaction 8 is rate determining, then the expression

$$-\frac{d[A]}{dt} = k_4[{}^1A^*][A]$$

should dominate the observed kinetics. If it is assumed that $[{}^1A^*]$ is constant, *i.e.*, steady-state conditions, the rate of reaction becomes

$$\text{rate} = k'[A]$$

which is first order.

Using the integrated form of the first-order rate expression

$$kt = \log\left[\frac{a}{a - x}\right]$$

where a is the initial concentration of anthracene and $a - x$ is the concentration of anthracene at time t, a plot of $\log [a/(a - x)]$ *vs.* t should be linear. Such a plot is linear at low conversions while there is a deviation from linearity in the region corresponding to conversions of 3–4% and larger of anthracene to photodimer. This is indicative of a decrease in the rate of photodimerization with irradiation time.

This deviation from linearity raises the question as to the nature of the dispersion of the anthracene in the polystyrene film and the feasibility of its diffusion within the polymer. Some idea of the nature of the dispersion is to be found in an examination of the ultraviolet spectra of anthracene in benzene, in polystyrene film, and in a potassium bromide pellet. These spectra are shown in Figure 2, and the positions of the absorption maxima with respect to the different environments at 25° are given in Table III.

Table III. Influence of Environment on the Anthracene Absorption Spectrum at 25°

Environment	Wavelength, Å			
Liquid C_6H_6	3255	3415	3590	3785
Polystyrene	3265	3425	3600	3800
KBr	3350	3530	3720	3930
Monocrystals[a]		3530	3725	3930

[a] A. Bree and L. E. Lyons, *J. Chem. Soc.*, 2662 (1956).

We now feel that anthracene is dispersed in potassium bromide in the form of microcrystals and that photodimerization probably takes place at distortions on the surface of the crystals and works its way into the crys-

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(15) R. Livingston and V. Subba Rao, *J. Phys. Chem.*, 63, 794 (1959).

tals.[16] The fact that in polystyrene, or in poly(methyl methacrylate) for that matter, the position of the absorption maxima and the shape of the absorption band are almost the same as in fluid benzene solutions indicates that the distribution is essentially homogeneous and not crystalline, in agreement with observations of other workers in related systems.[3f,4c] The slight red shift is ascribed to the less polar environment of the polymer compared to the benzene solution.

When the film was subjected to a high vacuum for 96 hr, there was always a reduction in the anthracene concentration of about 4-5%, indicative of diffusion of anthracene near the surface of the film out of the film. Thus some slight mobility of the anthracene is indicated. It was also possible *via* prolonged irradiation to convert a high percentage of the anthracene to photodimer. There were no indications that there would be an abrupt cessation of dimerization as soon as all anthracene molecules in a favorable position for dimerization had reacted, with further dimerization restricted because of the lack of mobility of the residual anthracene within the film.

If there were residual benzene within the film, the anthracene could be visualized as a very concentrated fluid solution with consequent anthracene mobility. If this were true, then it would seem reasonable to expect that the values of the quantum yields should be of the same order as in a typical fluid solution. For similar anthracene concentrations, the quantum yields measured in fluid solution were at least two orders of magnitude larger[14] than those we have measured in polystyrene. The latter values are even less than those obtained for similar anthracene concentrations in potassium bromide pellets.[7] This further indicates that there is no appreciable aggregation in the film. Furthermore, it suggests that there is not sufficient residual benzene in the film to give the anthracene any appreciable mobility.

Thus, we envisage a situation in which the polymer film consists of a series of channels and cavities, which could possibly be related to areas of irregular packing of the polymer chains, in which the anthracene is constrained, but in which it has a certain, albeit very small, mobility. Those anthracene molecules in the most favorable positions would undergo dimerization first, followed by dimerization of those in less favorable positions by virtue of their remoteness from each other. Hence, one would expect the rate of photodimerization to fall off slowly as the irradiation proceeds. This was, in fact, observed.

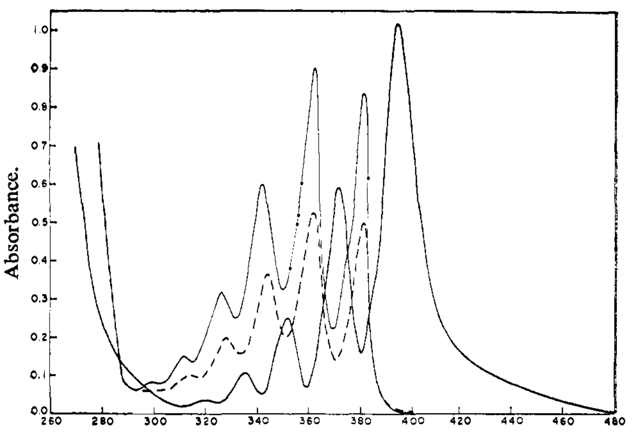

Figure 2. Absorption spectra of anthracene in various environments: ———, liquid benzene; – – – –, polystyrene; ———, potassium bromide pellet.

Mechanism of Photooxidation. The formation of photoperoxides has received intensive study during the past decade in order to attempt to resolve the nature of the intermediates involved. Most of the recent workers[17] favor the Kautsky mechanism[18] involving singlet oxygen as the reactive intermediate which gives the photoperoxide. Other workers[15] have suggested the presence of a biradical type "moloxide" as the intermediate. Actually, the over-all kinetic schemes are identical, differing only in the nature of the intermediates. We prefer the singlet oxygen hypothesis, and a simplified mechanism employing this is shown in eq 9-15. In this mechanism, A, $^1A^*$, and $^3A^*$ refer

$$\begin{array}{rlr}
A + h\nu \longrightarrow {}^1A^* & I_a & (9)\\
{}^1A^* \longrightarrow A + \text{"energy"} & k_1 & (10)\\
{}^1A^* \longrightarrow {}^3A^* & k_2 & (11)\\
{}^3A^* \longrightarrow A + \text{"energy"} & k_3 & (12)\\
{}^3A^* + O_2 \longrightarrow A + {}^1O_2 & k_5 & (13)\\
{}^1O_2 + A \longrightarrow AO_2 & k_6 & (14)\\
{}^1O_2 \longrightarrow O_2 + \text{"energy"} & k_7 & (15)
\end{array}$$

to anthracene in its ground, excited-singlet, and excited-triplet states, respectively. AO_2 is the photoperoxide and $^1O_2$ is singlet oxygen (either $^1\Delta_g$ or $^1\Sigma_g$). Equations 10, 12, and 15 refer to all photophysical processes by which anthracene or oxygen can return to ground state. The photodimerization reaction has been left out in the treatment of our kinetic data because the quantum yield of photooxidation is at least ten times greater under the same reaction conditions (see Table II). Thus, the measured quantum yield of anthracene disappearance, $\Phi_{-A'}$, is taken as the quantum yield of photooxidation, Φ_{AO_2}.

Making the usual steady-state approximations, the following expression can be derived for the quantum yield of photooxidation Φ_{AO_2}.

$$\Phi_{-A'} = \Phi_{AO_2} = \frac{k_2k_5k_6[O_2]}{(k_1 + k_2)(k_3 + k_5[O_2])(k_6[A] + k_7)}[A]$$

If $k_6[A] << k_7$ and $[O_2]$ is constant, then the quantum yield expression reduces to

$$\Phi_{-A'} = \alpha[A]$$

where

$$\alpha = \frac{k_2k_5k_6[O_2]}{(k_1 + k_2)(k_3 + k_5[O_2])(k_6[A] + k_7)}$$

The plot of $\Phi_{-A'}$ *vs.* [A] should be a straight line and pass through the origin. This plot is indeed linear, passing through the origin. The value of the slope is 1.035 M^{-1}. If $[O_2]$ is indeed constant and the formation of

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(16) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **45**, 3564 (1966).

(17) For a recent review, see K. Gollnick and G. O. Schenk, Chapter 10, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1967.

(18) H. Kautsky and H. de Bruyn, *Naturwissenschaften*, **19**, 1043 (1931).

the photoperoxide is independent of the rate of diffusion of oxygen into the film, the rate of conversion of anthracene to photoperoxide will be constant.

The plot of the integrated first-order expression, $kt = \log [a/(a - x)]$, of the change of the anthracene concentration as a function of irradiation time is linear and shows that the photoperoxide is being produced at a constant rate over the extent of reaction studied (10–12% conversion of anthracene to photoperoxide). Experiments will be conducted in the near future in an attempt to determine if singlet oxygen is indeed the reactive intermediate using an atmosphere rich in singlet oxygen.

In conclusion, we note that the use of potassium bromide pellets as an ideal medium for studies of photobiological significance has been suggested[19] in view of the physical relationship between such environments and the heterogeneous environment of the potassium bromide pellet. It is very possible that the environment within polymer films is even more closely related to that in photobiological systems, a view also held by other workers,[3f] and the increasing use of polymer films for such studies is envisaged in the near future.

Acknowledgments. The authors wish to express their thanks to the Polymer Chemistry Section, American Cyanamid Co., and in particular Dr. R. L. Kugel and Mr. R. Walker, for supplying polymer films with which the first qualitative studies were made. The continuing helpful interest of Mr. D. Burley in this research is gratefully acknowledged. This research was supported by Grant AP 00109, National Center for Air Pollution Control.

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The Reaction of Amines with Haloalkanes. I. The Photochemical Reaction of *n*-Butylamine with Carbon Tetrachloride

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Contribution from the John Harrison Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104. Received September 30, 1967

Abstract: Reaction between *n*-butylamine and carbon tetrachloride at room temperature and in the absence of oxygen can be initiated by ultraviolet light, by visible light at certain concentrations of amine, or by Cu(I) or Fe(II) salts. The major products of the 2537-Å photolysis of solutions of *n*-butylamine in CCl_4 in the absence of oxygen at 30° are amine hydrochloride, chloroform, hexachloroethane, butylidenebutylamine, and ammonia. Quantum yields varying from 1 to 100 are explained in terms of a free-radical chain reaction initiated by the absorption of light by the charge-transfer complex of *n*-butylamine with CCl_4 and propagated by trichloromethyl and dehydrogenated amine radicals. The presence of oxygen has a great effect on the rate and course of the photochemical reaction probably because the oxygen reacts with the trichloromethyl radicals.

The reaction of amines with halomethanes, especially the reaction of primary amines with carbon tetrachloride under surprisingly mild conditions, has received considerable attention recently.[1–12] Amines have been shown to form charge-transfer complexes with halomethanes, and this complex formation has been given as the cause of the photochemical instability of solutions of amines in halomethanes.[7,10,12] Other studies[2,3,6,9,10] have found that metals, metal salts, and oxygen can have a great effect on the rapidity and course of the reaction. Both ionic and free-radical mechanisms have been put forward to explain the experimental results, but no agreement has been obtained on the nature of the separate or combined effects of the several factors affecting the reaction. Up to the present, the findings have been fragmentary and rather qualitative in nature. For example, the effect of oxygen has been studied largely by the exclusion or admission of air, and quantitative kinetic studies are almost completely lacking. In the investigation reported below, we have started a systematic quantitative study of the reaction, beginning with the effects of light radiation and oxygen.

The *n*-butylamine was chosen as amine not only because of its simple structure, but also because of its convenient physical properties. It has nearly the same vapor pressure as carbon tetrachloride and its good solvent properties eliminate the need of an extra solvent that might cause complicating side reactions.

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