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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**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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## Experimental Section

**General Considerations.** Much confusion has occurred in the research on the amine–carbon tetrachloride reaction due to the general lack of appreciation of the unusual sensitivity of that reaction to oxygen, light (both visible and ultraviolet), concentration of reactants, and metallic impurities. All four of these variables greatly affect the reaction rate and the kinds and proportions of the products obtained. The authors speak from considerable and difficult experience in this regard. For example, we have encountered many puzzling differences in reaction rates which were eventually traced to the use of syringes containing concealed brass parts and to the use of Teflon-coated stirring bars that had picked up traces of metal salts during use in other reaction systems.

Furthermore, visible light initiates reaction when the *n*-butylamine concentration exceeds the moderate concentration of 0.4 *M*, since at such concentrations the solutions absorb appreciably in the visible region. Oxygen greatly increases the rate of reaction once initiation has been caused by light radiation or metal salts. Dilute solutions of the amine in $CCl_4$ when exposed to air and daylight show induction periods of at least 3-hr length and then react rapidly. These induction periods can be eliminated in the presence of an atmosphere of oxygen by addition of trace amounts of cuprous or ferrous salts or a small amount of ultraviolet radiation. On the other hand, complete exclusion of oxygen, light, metals, and metal salts appears to prevent reaction even at high amine concentration.

**Materials.** Reagent grade *n*-butylamine (Matheson Coleman and Bell) was distilled (76.7°) over molecular sieves and was stored over molecular sieves. Reagent grade $CCl_4$ (Baker) was treated similarly (bp 77.0°). For the spectrophotometric studies, the same butylamine was used but the cyclohexane and $CCl_4$ were both Spectrograde (Matheson Coleman and Bell) and were dried over molecular sieves. The sieves were Linde Type 4A in all cases.

Styrene (Baker, stabilized with *t*-butylpyrocatechol) was distilled at 30° (10 torr). Ammonia (Matheson) was used directly from a conventional lecture bottle. Airco oxygen was passed over Ascarite and Drierite before use.

Cuprous chloride (Baker, assay 94.9% CuCl) and ferrous ammonium sulfate (Baker, assay 99.4% $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) were used without further purification. 9,10-Dihydroanthracene (K & K Laboratories) was crystallized from ethanol (mp 108–109°; lit.[13] 109.5–110.0°). Hydroquinone (Baker, mp 172–174°) and hexachlorothane (Matheson Coleman and Bell, mp 185–186°) were used without further purification.

Butylidenebutylamine ($C_3H_7CH{=}NC_4H_9$) was prepared and purified by the method of Day and Stein[14] (bp 140–143°, lit.[15] 140–145°; $n^{25}$D 1.4188, lit.[15] $n^{20}$D 1.4211). It was found to be better than 98% pure by glpc.

*n*-Butyl isocyanide was prepared by the method of Ugi and Meyr.[16] The material boiling at 120–123° was used to obtain the infrared spectrum of a 5% (by volume) solution in $CCl_4$. An outstanding feature of the spectrum was a narrow, intense band at 2140 $cm^{-1}$.

**Preparation of Samples.** For the reactions in the absence of oxygen, *n*-butylamine and $CCl_4$ ampoules were separately degassed by several freeze–pump–thaw cycles and then distilled consecutively into the reaction cell and pumped and sealed while frozen by liquid nitrogen. The reaction cell was quickly brought to room temperature for irradiation.

For those experiments where oxygen was used, dried oxygen was added directly to the degassed $CCl_4$ in the cell. Liquid amine which had been saturated with oxygen was then added by syringe through a septum.

**Analyses.** After irradiation, aliquot samples were drawn from the reaction cell and quenched with aqueous acid. The organic layer of these quenched samples was analyzed by vapor phase chromatography for $CHCl_3$ and $C_2Cl_6$. Chloride ion was determined in the aqueous phase by Volhard titration with silver nitrate. The other products, except N,N′-di-*n*-butylurea, were determined directly and rapidly from aliquots of the reacting system by vapor phase chromatography using a flame ionization detector.

The following columns were used: $C_2Cl_6$–silicone gum rubber on Chromosorb-W, at 135°; $CHCl_3$–15% silicone oil (Dow Corning 200) on Chromosorb-W, at ambient temperature; butylidenebutylamine–20% Dowfax 9N9 on KOH-treated Chrom P, 60–80 mesh, at 110°; $NH_3$–20% Dowfax 9N9 on KOH-treated Chrom P, 60–80 mesh, at 70°.

N,N′-Di-*n*-butylurea precipitated in large amount (*e.g.*, 8.5% of amine was converted into the urea in a 1.1 *M* amine solution in 24 hr) in oxygenated systems when the aliquots were quenched with aqueous acid. It was removed and recrystallized from ethanol (mp 72°, lit.[17] 71°).

*Anal.* Calcd for $C_9H_{20}ON_2$: C, 62.75; H, 11.70; N, 16.26; O, 9.29. Found: C, 62.71; H, 11.44; N, 16.27; O, 9.29.

No additional chlorinated products were detected. Although the misleadingly[3] strong odor of *n*-butyl isocyanide was present in the reacted systems, the actual amount of isocyanide present was so small that it could not be detected by chromatography or by infrared spectrophotometry.

**Quantum Yields.** The photochemical reaction cell was constructed about a U.V. Products low-pressure immersion-type mercury arc equipped with a 24/40 ground joint by which it entered the reaction vessel so that the liquid in that vessel surrounded the arc tube to any desired length. The reaction vessel held up to 70 ml of liquid and was equipped for magnetic stirring and had attachments for sample removal and for connection with the vacuum line and manometer system.[18]

The cell was immersed in a constant-temperature water bath at 30 ± 0.03°. The irradiation periods were 5–10 min in length. Measurements of $CCl_4$ alone in these cells showed that the temperature was maintained at 30° during irradiation.

Correction for the effect of visible light was made by determining the extent of reaction in blank runs carried out without ultraviolet irradiation. The correction usually amounted to only about 1 to 2% of the total. The quantum yield at the initial amine concentration was obtained by extrapolating to zero time the quantum yields determined at the several stages of any run. Approximately 90% of the output of the lamp was at 2537 Å, with small intensities at longer wavelengths, and the calculations were based on the assumption that the light was entirely 2537 Å light.

The light intensity entering the cell was determined by potassium ferrioxalate actinometry.[19] The intensity was varied by changing the volume of solution in the cell, whereby different lengths of the immersion lamp were surrounded by the liquid. The volumes of solution were varied from 9 to 63 ml. Preliminary experiments showed that the quantum yields were independent of the volume of liquid at constant amount of exposure to the lamp. Constant stirring rates, determined to produce the maximum quantum yield, were used. The reacting solutions were always sufficiently concentrated to absorb 100% of the incident light.

Amine concentrations greater than 0.4 *M* were used in most cases. This prevented precipitation during irradiation, since the amine helps to keep in solution the butylamine hydrochloride produced.

For the studies using visible light of higher intensity (see Table III), the photochemical cell was irradiated from without by the light of a 300-w incandescent bulb filtered through Pyrex.

When oxygen was added, its pressure above the reaction system was measured with an open-end manometer containing dibutyl phthalate. The amount of oxygen consumed was calculated from the starting amount and from the measured partial pressure at the time, employing Henry's law and assuming the solubility of the oxygen was the same as in pure $CCl_4$ at 30° (0.0116 *M* at 1 atm).[20]

**Ultraviolet Spectroscopy.** Complex formation between the amine and $CCl_4$ was studied by ultraviolet spectroscopy, using solutions of these substances in cyclohexane. The components were purged with nitrogen before mixing. Amine concentration was determined by titration with standard acid. All of the measurements were made with 1-cm stoppered silica cells in a Beckman Model DK-1 recording spectrophotometer at 25–26°, with pure solvent serving as a reference. Since the amine reacted with the $CCl_4$ because of the radiation, the absorbancy values were obtained by extrapolating optical density–time plots back to zero time.

## Results and Discussion

**Complex Formation.** The ultraviolet absorption spectra of cyclohexane solutions of *n*-butylamine and

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**Table I.** Quantum Yields of Products at 2537 Å and 30°

| Reactants, $M$ | | | Initial quantum yields | | | | |
|---|---|---|---|---|---|---|---|
| Amine | $CCl_4$ | $I_0$[a] | $RNH_3Cl$ | $CHCl_3$ | $C_2Cl_6$ | R'CH=NR | $NH_3$ |
| 0.198 | 10.16 | 6.97 | 3.50 | 2.15 | 0.98 | 2.48 | n[b] |
| 0.450 | 9.90 | 6.97 | 15.1 | 10.8 | 2.15 | 10.64 | n |
| 1.12 | 9.22 | 6.97 | 32.4 | 23.7 | 3.27 | 22.6 | n |
| 2.25 | 8.06 | 6.97 | 60.7 | 45.9 | 6.69 | 57.4 | 40.8 |
| 4.50 | 5.76 | 6.97 | 113. | 96.1 | 9.32 | 95.2 | 79.2 |
| 1.12 | 9.22 | 0.76 | 83.5 | 79.0 | 2.63 | n | n |
| 1.12 | 9.22 | 2.00 | 60.3 | 51.0 | 3.75 | n | n |
| 1.12 | 9.22 | 9.40 | 25.3 | 20.9 | 3.00 | n | n |
| 0.450[c] | 9.90 | 6.97 | 13.6 | 8.40 | 1.80 | n | n |
| 0.450[d] | 9.90 | 6.97 | 65.1 | 0.72 | 0.53 | 14.4 | 10.3 |

[a] $I_0$ = incident intensity in quanta $sec^{-1}$ $cc^{-1}$ × $10^{-14}$. [b] n = not determined. [c] $O_2$ pressure, 100 torr. [d] $O_2$ pressure, 617 torr.

carbon tetrachloride show that the amine forms a complex with $CCl_4$ that is a 1:1 charge-transfer complex or that the amine and $CCl_4$ interact in 1:1 pairs to give rise to so-called contact charge-transfer spectra.[21] Infrared spectroscopic and vapor pressure measurements by other workers[22–24] on other amine–halomethane complexes indicated that they are of the type formed between pyridine and iodine.

Figure 1 shows that for *n*-butylamine and $CCl_4$ the charge-transfer band appears in the spectral region where both free components absorb. For this reason, calculations were based on absorbancy readings at the side of the spectral band. A maximum was shown at a mole fraction of 0.5 in a continuous-variation[25] plot, and the Benesi–Hildebrand[26] relation for 1:1 complex formation was obeyed (Figure 2). The values of $K\epsilon$, where $\epsilon$ and $K$ are the molar extinction coefficient and the equilibrium constant for the formation of the complex, respectively, were obtained at each of the frequencies shown in Figure 2, but accurate determination of the equilibrium constant, $K$, was not possible as shown by the nearly zero intercepts; however, the weakness of the complex formation is certain. Similar results were obtained by application of the Rose–Drago[27] relation.

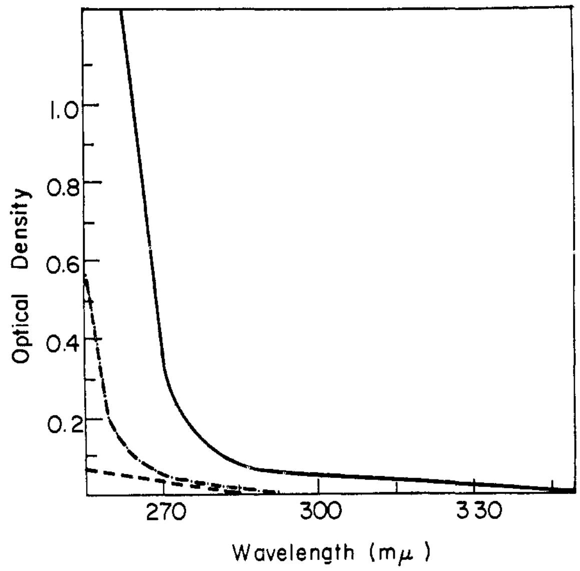

Figure 1. Typical solution spectra of *n*-butylamine and $CCl_4$ in cyclohexane: – – –, pure amine (0.340 $M$); – · –, pure $CCl_4$ (1.39 $M$); ———, mixture (0.340 $M$ amine and 1.39 $M$ $CCl_4$).

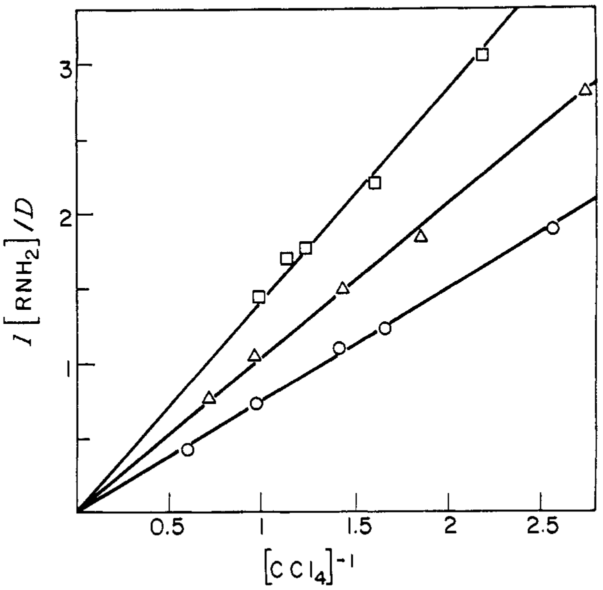

Figure 2. Benesi–Hildebrand plots for *n*-butylamine–$CCl_4$ in cyclohexane at 25°: ○, 265 mμ ($K\epsilon$ = 1.35 ± 0.2); △, 270 mμ ($K\epsilon$ = 0.95 ± 0.2); □, 275 mμ ($K\epsilon$ = 0.70 ± 0.2).

**Photochemical Reaction in the Absence of Oxygen.** The initial quantum yields found in the photochemical experiments are listed in Table I. The individual experiments were reproducible to approximately ±10%. The photochemical reaction at 2537 Å has a quantum yield of about 1 to 100, depending on experimental conditions; although reaction is initiated photochemically, it continues by a nonphotochemical chain process.

The rate of formation of chloroform varies as the half-power of the light intensity (Figure 3), which suggests a second-order terminating step. The rate of formation of hexachloroethane varies as the first power of the light intensity (Figure 4). Table II and Figure 5 show the

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(22) P. Datta and G. M. Barrow, *ibid.*, **87**, 3053 (1965).

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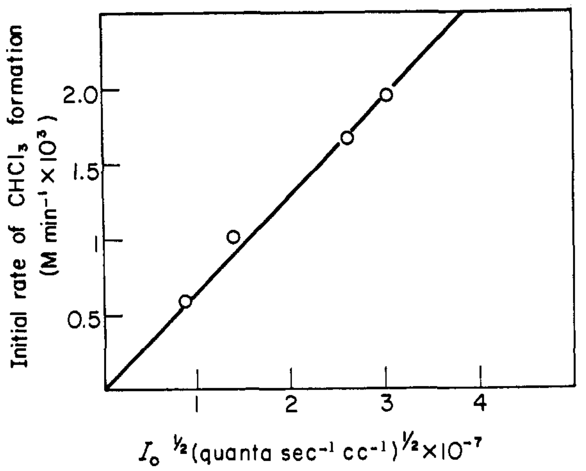

Figure 3. Variation of initial rate of formation of chloroform with the square root of light intensity at 1.1 $M$ amine.

rates of formation of the major products in a typical run.

Table II. Product Yields in the Photolysis of 2.25 $M$ Amine in CCl$_4$[a]

| Product, $M \times 10^2$ | Time, min 5 | 10 | 20 | 30 | Extrap quantum yield |
|---|---|---|---|---|---|
| $n$-Butylamine hydrochloride | 1.85 | 3.41 | 5.66 | 7.69 | 60.7 |
| Chloroform | 1.38 | 2.54 | 3.92 | 4.93 | 45.9 |
| Hexachloroethane | 0.290 | 0.412 | 0.700 | 0.973 | 6.69 |
| Butylidenebutylamine | 1.60 | 3.05 | 4.81 | 5.85 | 57.4 |
| Ammonia | 1.25 | 2.14 | 3.25 | 3.82 | 40.8 |

[a] At 6.97 × 10$^{14}$ quanta sec$^{-1}$ cc$^{-1}$.

In the concentration range where the complex absorbs visible light, *i.e.*, at amine concentrations greater than 0.4 $M$, reaction is initiated by visible light (Table III). Addition of 9,10-dihydroanthracene or styrene reduces the rate greatly. The dihydroanthracene and styrene are known as efficient scavengers for trichloromethyl radicals[28,29] and the magnitude of the inhibition caused in these reactions argues strongly that the photochemical reaction is a radical process with a chain length of the order of 10. Hydroquinone at concentrations not exceeding that of the amine does not affect the quantum yield of the photochemical reaction. Bonner and Hancock[11] found that hydroquinone did not inhibit the reaction of benzylamine with carbon tetrachloride, but it was noted by Asscher and Vofsi[6] that this is not evidence against the free-radical reaction since hydroquinone is by no means a universal inhibitor.[30]

Table III. Effect of Added Substances on Products Formed in 60 Min in the Reaction of 4.5 $M$ Amine in CCl$_4$ in the Absence of Oxygen

| Added substance | Product, $M \times 10^2$ CHCl$_3$ | RNH$_3$-Cl | C$_2$Cl$_6$ | R'CH=NR |
|---|---|---|---|---|
| None (visible light) | 2.1 | 1.7 | *a* | 1.4 |
| Styrene (0.2 $M$, visible light) | 0.088 | <0.1 | *a* | 0.02 |
| 9,10-Dihydroanthracene (1 $M$, visible light) | 0.52 | 0.6 | *a* | 0.2 |
| Hydroquinone (1 $M$, visible light) | 1.9 | 1.8 | *a* | 1.3 |
| CuCl (satd soln, in the dark) | 9.0 | 10.0 | 0.04 | 8.0 |
| Ferrous ammonium sulfate (satd soln, in the dark) | 15.0 | 17.0 | 0.09 | 14.0 |

[a] Negligible amount

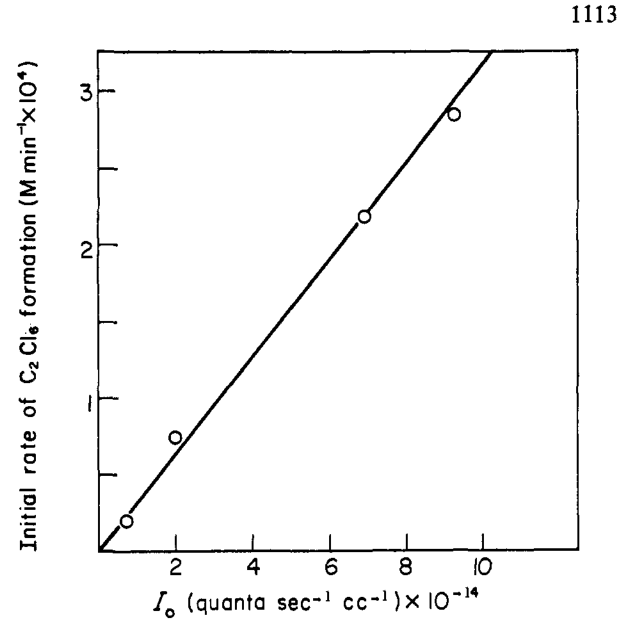

Figure 4. Variation of initial rate of formation of hexachloroethane with light intensity at 1.1 $M$ amine.

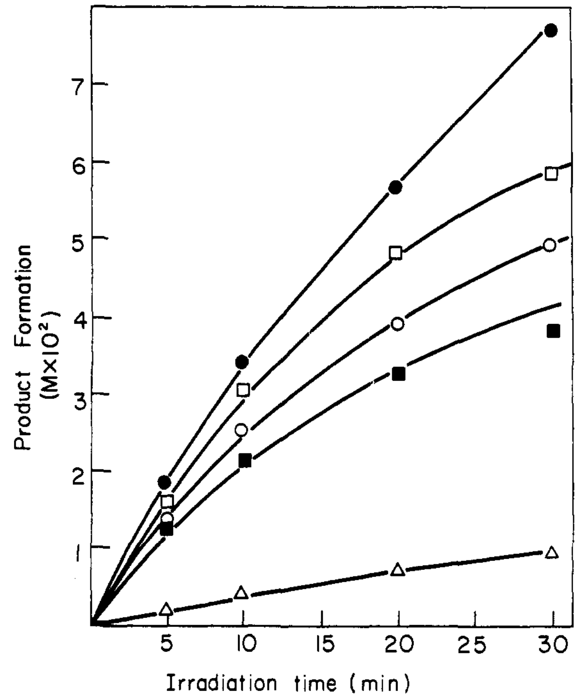

Figure 5. Product formation as a function of irradiation time for 2.25 $M$ amine: ●, HCl; ○, CHCl$_3$; △, C$_2$Cl$_6$; □, R'CH=NR; ■, NH$_3$.

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(28) E. C. Kooyman, *Discussions Faraday Soc.*, **10**, 163 (1951).
(29) J. G. Robb and D. Vofsi, *Trans. Faraday Soc.*, **55**, 568 (1959).

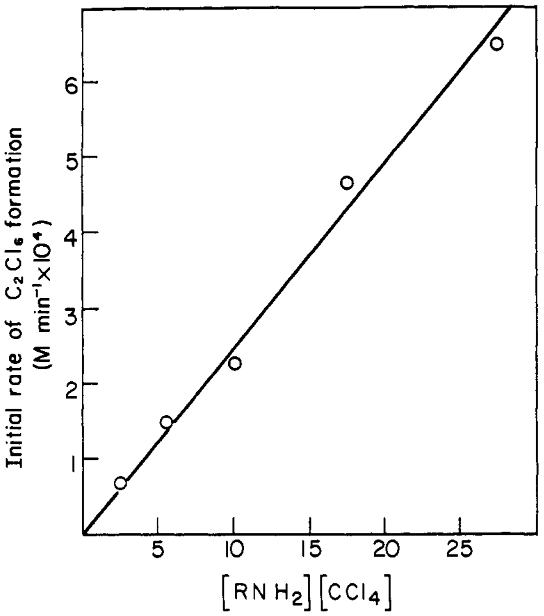

Figure 6. Variation in initial rate of $C_2Cl_6$ formation with $[RNH_2]\cdot[CCl_4]$ at constant intensity.

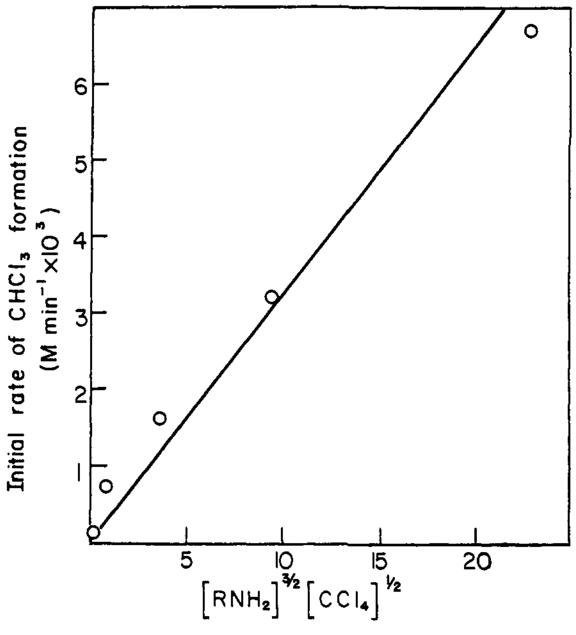

Figure 7. Variation of initial rate of $CHCl_3$ formation with $[RNH_2]^{3/2}[CCl_4]^{1/2}$ at constant intensity.

The results support the view that the process of chain initiation is through decomposition of the charge-transfer complex. At 2537 Å and with visible light and at the concentrations used, the homolytic dissociation of either $CCl_4$ or *n*-butylamine separately is unlikely because of their low extinction coefficients as compared with that of the charge-transfer complex. Stevenson and Coppinger[7] and Kim[8] have suggested that the complex dissociates photochemically into $RNH_2^+Cl^-$ and $\cdot CCl_3$. The trichloromethyl radical may then abstract a hydrogen atom from the amine, while the $RNH_2^+Cl^-$ may also react with amine, losing HCl to form a $R\dot{N}H$ radical.

$$RNH_2\cdot CCl_4 + h\nu \longrightarrow RNH_2^+Cl^- + \cdot CCl_3 \quad (1)$$

$$RNH_2^+Cl^- + RNH_2 \longrightarrow RNH_3Cl + R\dot{N}H \quad (2)$$

Chain propagation and termination could then proceed by the following route, which is similar to that suggested by Kurz, Hutton, and Westheimer[31] for the chain reaction that occurs in the photochemical reduction of bromotrichloromethane by derivatives of 1,4-dihydropyridine.

$$\cdot CCl_3 + RNH_2 \longrightarrow CHCl_3 + R\dot{N}H \text{ (or } R'\dot{C}HNH_2) \quad (3)$$

$$R\dot{N}H \text{ (or } R'\dot{C}HNH_2) + CCl_4 \longrightarrow RNClH \text{ (or } R'CHClNH_2) + \cdot CCl_3 \quad (4)$$

$$RNClH \text{ (or } R'CHClNH_2) + RNH_2 \longrightarrow R'CH{=}NH + RNH_3Cl \quad (5)$$

$$R'CH{=}NH + RNH_2 \longrightarrow R'CH{=}NR + NH_3 \quad (6)$$

$$2\cdot CCl_3 \longrightarrow C_2Cl_6 \quad (7)$$

Steps 4 and 5 have been suggested by Asscher and Vofsi[6] for the reaction catalyzed by metal salt. The reaction of the imine, R'CH=NH, with excess amine to give butylidenebutylamine, R'CH=NR, has been suggested by many workers.

The relative values of the quantum yields of the different products given in Table I support the mechanism. Thus, for the reactions carried out in the absence of oxygen, the quantum yield of the HCl, *i.e.*, of the $RNH_3Cl$, is closely equal to the yield of chloroform plus twice the yield of hexachloroethane. The less accurate determinations of the yield of butylidenebutylamine may also be used to inspect the mechanism. The yield of butylidenebutylamine is roughly equal to one-half the sum of the yields of the HCl and chloroform, as is also expected.

The absence of additional chlorinated products and the small size of the amount of isocyanide formed show that the reaction is not complicated by extensive side reactions due to the formation of such radicals as $CCl_3^-$ or $:CCl_2$ in important amounts.

Furthermore, the yield of HCl produced by step 5 should be equal to the yield of butylidenebutylamine and also equal to the sum of the yields of the chloroform and the HCl produced in step 2. From these relationships and the others given above, we see that step 2 has a quantum yield of slightly less than unity at an amine concentration of 0.2 *M* and that this yield increases with amine concentration. The yield of step 2 does not appear to be affected greatly by the intensity of the radiation.

Assuming steady-state concentrations for the $R\dot{N}H$ (or $R'\dot{C}HNH_2$) and $\cdot CCl_3$ radicals, the mechanism yields the following rate expressions which agree with the experimental results given in Table IV (Figures 3, 4, 6, and 7).

$$d[C_2Cl_6]/dt = kI[RNH_2][CCl_4]$$

$$d[CHCl_3]/dt = k'I^{1/2}[RNH_2]^{3/2}[CCl_4]^{1/2}$$

Further experimentation will no doubt yield independent evidence for the mechanism or for modification of its details as given in the seven steps written above.

**Effect of Metal Salts.** The Cu(I) and Fe(II) salts initiated reaction in the dark and in the absence of oxy-

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(30) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 168, 175.

(31) J. L. Kurz, R. Hutton, and F. H. Westheimer, *J. Am. Chem. Soc.*, 83, 584 (1961).

**Table IV.** Variation of the Rates of $CHCl_3$ and $C_2Cl_6$ Formation with Concentration and Light Intensity

| Reactants, *M* | | | Rates | |
|---|---|---|---|---|
| Amine | $CCl_4$ | $I_0$[a] | $C_2Cl_6$[b] | $CHCl_3$[c] |
| 0.198 | 10.16 | 6.97 | 0.68 | 0.15 |
| 0.450 | 9.90 | 6.97 | 1.50 | 0.75 |
| 1.12 | 9.22 | 6.97 | 2.28 | 1.65 |
| 2.25 | 8.06 | 6.97 | 4.66 | 3.20 |
| 4.50 | 5.76 | 6.97 | 6.50 | 6.70 |
| 1.12 | 9.22 | 0.76 | 0.20 | 0.60 |
| 1.12 | 9.22 | 2.00 | 0.75 | 1.02 |
| 1.12 | 9.22 | 9.40 | 2.82 | 1.97 |

[a] $I_0$ = incident intensity in quanta $sec^{-1}$ $cc^{-1}$ $\times 10^{-14}$. [b] Initial rate, $M$ $min^{-1} \times 10^4$. [c] Initial rate, $M$ $min^{-1} \times 10^3$.

gen. The molar product ratios found were similar to those of the photochemical reaction (*i.e.*, $3RNH_2 + CCl_4 \rightarrow R'CH{=}NR + NH_3 + RNH_3Cl + CHCl_3$). Small amounts of hexachloroethane were also present (Table III), indicating the presence of $\cdot CCl_3$ radicals in the system. There was no indication of induction periods. The reaction is inhibited by styrene.

Asscher and Vofsi[6] have shown that the reaction of triethanolamine with $CCl_4$ in the presence of cuprous and ferrous salts produces $\cdot CCl_3$ radicals through a ligand-transfer process, $Cu^+ + CCl_4 \rightarrow Cu^+(Cl) + \cdot CCl_3$. The propagation and termination steps appear to be the same as suggested in the photochemical reaction.

**Photochemical Reaction in the Presence of Oxygen.** As shown by the results at the bottom of Table I, the presence of oxygen changes the molar product ratios, and a new product, N,N′-dibutylurea, is formed. The yields of both $CHCl_3$ and $C_2Cl_6$ are reduced greatly, especially as the oxygen/amine concentration ratio is increased.

Oxygen is absorbed strongly (Table V). The formation of N,N′-dibutylurea is most probably the result of reaction of $\cdot CCl_3$ radicals with oxygen to yield phosgene which reacts rapidly with excess amine to form the urea[32] instead of chloroform or hexachloroethane.

$$\cdot CCl_3 + 0.5O_2 \longrightarrow COCl_2 + \cdot Cl$$

or

$$\cdot CCl_3 + O_2 \longrightarrow COCl_2 + \cdot ClO$$

$$COCl_2 + 2RNH_2 \longrightarrow CO(NHR)_2 + 2HCl$$

**Table V.** Product Yields in the Photolysis of 0.45 *M* Amine in $CCl_4$ under 617 Torr[a] of $O_2$

| | Product yields, $M \times 10^2$ | | | |
|---|---|---|---|---|
| Time, min | $RNH_3Cl$ | R′CH= NR | $NH_3$ | $O_2$ absorbed, $M \times 10^2$ |
| 5 | 2.20 | 0.65 | 0.34 | 0.46 |
| 10 | 4.05 | 0.90 | 0.72 | 0.81 |
| 20 | 7.61 | 1.85 | 1.25 | 1.68 |
| 30 | 9.98 | 2.24 | 1.46 | 1.93 |

[a] $I_0 = 6.97 \times 10^{14}$ quanta $sec^{-1}$ $cc^{-1}$.

The rate of the main reaction is not diminished by the oxygen as it is in the case of styrene addition where the radical produced from the styrene is apparently not chain sustaining. Table I shows that, apart from the side reaction forming the dibutylurea, the amine is converted largely into amine hydrochloride, butylidenebutylamine, and ammonia when the pressure of the oxygen is increased. Furthermore, the yields of those products are increased by the oxygen, which is probably due to the fact that the $\cdot Cl$ or $\cdot ClO$ radicals produced by the oxygen propagate the main chain by abstracting hydrogen from the amine.[33] The over-all stoichiometry of the photochemical reaction in the presence of oxygen appears to approach the following relationship as the oxygen pressure increases.

$$8RNH_2 + CCl_4 + 0.5O_2 \longrightarrow CO(NHR)_2 + 4RNH_3Cl + R'CH{=}NR + NH_3$$

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