

the original intensity reading to correct for impurity or by-product emission.

Acknowledgment. This research was supported in part by funds provided by the Food and Drug Ad-

ministration DHEW under Contract FDA 71-285 and the Michigan Agricultural Experiment Station, Michigan Agricultural Experiment Station Journal Article No. 6786.

Reaction of Amines with Haloalkanes. III. The Stability and Photochemical Decomposition of the Complex Formed by *n*-Butylamine with Carbon Tetrachloride

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Abstract: The formation constant for the 1:1 complex of *n*-butylamine and carbon tetrachloride has been measured by determination of its absorbance at 240–250 nm in *n*-hexane at 25°. The value of K_f was found to be 0.032 M^{-1} , a value placing the complex in the range of low stability shown by other aliphatic amine-haloalkane pairs. The limitation of the accuracy of that K_f value is discussed. An induction period in the photochemical decomposition of the complex aided the measurement of both K_f and the kinetics of the decomposition. The kinetic studies have been carried out in *n*-hexane at 25°, using both spectroscopic and chemical measurements. The results are in agreement with a mechanism proposed by Stevenson and Coppinger and by Mulliken for the decomposition of the weak complex and with a mechanism proposed for the photochemical initiation of chain reaction between the amine and haloalkane.

The photochemical initiation of reaction between amines and haloalkanes probably takes place by completion of charge transfer in the electron donor-acceptor interaction of the reactant molecules.¹⁻³ Spectroscopic measurements have shown that the complexes formed by that charge-transfer interaction are so loose as to approach the nature of contact pairs⁴ when the amines are aliphatic and CCl_4 is the acceptor,^{1,3,5,6} but no quantitative estimate of the strength of the complex involving a primary aliphatic amine has been made previously. Furthermore, although a reasonable mechanism for the decomposition of the excited complexes that form on light absorption has been suggested^{1,2} and has been related³ to the ensuing chain reaction, no experimental test of that mechanism has been made heretofore.

Since the complexes also appear to play an important role in dark initiations of the amine-haloalkane reactions,^{3,7,8} and since primary aliphatic amines have been used most frequently in the study of the reactions, we have made quantitative measurements of the stability and photochemical decomposition of the complex formed between *n*-butylamine and CCl_4 .

Experimental Section

Materials. Carbon tetrachloride and *n*-butylamine were prepared as before.³ Spectroquality *n*-hexane and chloroform (Matheson Coleman and Bell) were used as received. Purified nitrogen (Air Products, Inc.) was passed over Drierite before use. Ammonia gas (Air Products, Inc.) was used directly from a lecture bottle.

n-Butylamine hydrochloride (Eastman Organic Chemicals) was recrystallized from anhydrous ether. Hexachloroethane (Baker Chemical Co.) was used without further purification. *n*-Butyldenebutylamine was prepared by the method of Day and Stein⁹ (bp 141–145° (lit.¹⁰ 140–145°); n_D^{20} 1.4217 (lit.¹⁰ n_D^{20} 1.4211)). Potassium ferrioxalate was prepared by mixing three volumes of 1.5 M $K_2C_2O_4$ with one volume of 1.5 M $FeCl_3$ in the dark. The green precipitate was recrystallized three times from water and was stored in the dark.

Apparatus and Procedures. Dry prepurified nitrogen was bubbled through the amine and the CCl_4 for 2 hr to remove oxygen immediately before preparation of the solutions. The solvent used was *n*-hexane in all cases. Solutions were prepared in the dark and under nitrogen. Trials of degassing by several freeze-pump-thaw cycles produced no changes in the observations.

Concentrations were determined by weighing procedures. Smaller amounts of the reactants were delivered by syringes chosen to be free of initiating metals or salts.

A Cary Model 14 recording spectrophotometer was employed for all of the spectroscopic measurements. The stoppered cuvettes were kept at constant temperature by circulating water from a Wilkens-Anderson Lo Temp thermostat through their jackets. A stream of nitrogen was used to purge the cell compartment and to drive a magnetic stirrer placed under the cuvettes.

The intensity of the light entering the cells in the kinetic runs was determined by ferrioxalate actinometry suitable to the low intensity¹¹ used.

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For determination of the rate of chloride ion formation, aliquots were quenched with sulfuric acid at recorded times and were titrated by the Mohr method. The procedure was checked by determinations with pure *n*-butylamine hydrochloride.

Results

Formation Constant of the Complex. The formation constant, K_f , was measured at 25° in *n*-hexane solution. In an amine-haloalkane system, as in other systems of amines with weak acceptors, charge-transfer interaction produces a new band lying so close to the $n \rightarrow \sigma^*$ band of the donor amine that its maximum is hidden when the amine is in excess.^{1,3,5,6,12} That the new band is due to charge-transfer (CT) interaction has been demonstrated convincingly when the amine is aliphatic and the haloalkane is chloroform, fluorotrichloromethane, bromotrichloromethane, or CCl_4 .^{1,5,6} The absorption of that CT band is greater than the sum of the absorptions of the separate free components and Bittrich and Schütze⁶ have shown that the small effect of temperature on the absorbance is in the direction expected for complex formation rather than for contact-pair interaction. In the case of the *n*-butylamine- CCl_4 system it has been found^{8,13} that the absorption band shows the same behaviors as used to characterize the bands of the other aliphatic amine-haloalkane systems.

High excess concentrations of the donor were used in an attempt to follow Person's rule¹⁴ that the donor concentration should lie in the region 0.1 to 9.0 K_f^{-1} . The CCl_4 was kept at 0.0104 *M* and the amine was varied from 3.03 to 7.08 *M* in seven well-spaced concentrations. With such large excess of amine it was possible to compensate for its absorption experimentally.¹⁵ The seven solutions were each measured over the region 240–250 nm, which was chosen to provide maximum absorbance free of danger of the total absorbance due to amine at lower wavelengths. It is interesting that the rapidity of the reaction of primary amines with haloalkanes has discouraged⁵ efforts to determine the formation constants of the complexes formed by those amines. Fortunately, for the conditions used here, the systems were stable for a conveniently long induction period of at least 10 min before photochemical decomposition caused change in their absorbance.

The absorbance data were analyzed by the Liptay-Scott procedure.^{16–18} The ζ matrix showed that the relative absorbance at each wavelength did not vary greatly from its average with change in concentration (Table I).

The formation constant and molar absorptivities are shown in Table II. The mean value of K_f is 0.032 M^{-1} . The precision of the measurements is expressed by standard deviations determined by a least-squares procedure. The true accuracy of the K_f value will be discussed below.

Kinetic Studies. The induction period that permitted determination of K_f was measured for a series of

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Table I. Relative Absorbance (ζ_i) Values Using the 250-nm Absorbance as Reference

[RNH ₂], <i>M</i>	ζ_{245}	$\zeta_{242.5}$	ζ_{240}
3.03	1.625	2.012	2.225
3.54	1.686	2.116	2.384
4.04	1.683	2.113	2.316
4.55	1.833	2.231	2.333
5.06	1.710	2.089	2.322
6.07	1.636	2.014	2.286
7.08	1.550	1.900	2.228
$\bar{\zeta}_i$	1.675	2.068	2.299

Table II. The Formation Constant, K_f , and Molar Absorptivities, ϵ_λ , of the *n*-Butylamine- CCl_4 Complex at 25° in *n*-Hexane

λ , nm	K_f , M^{-1}	ϵ_λ , $M^{-1} \text{ cm}^{-1}$
250.0	0.037 ± 0.007	752 ± 116
245.0	0.031 ± 0.005	1478 ± 204
242.5	0.027 ± 0.006	2060 ± 412
240.0	0.034 ± 0.008	1852 ± 370

nine solutions in *n*-hexane at a constant CCl_4 concentration of 0.01036 *M*, with the amine concentration varying from 0.303 to 1.912 *M*. The absorbance was recorded carefully at 250 nm at 25° over a period extending well beyond the end of induction, which was marked sharply by onset of a rise in absorbance. The mean value of the induction time was 16.1 min for the series, with a standard deviation of ±1.1 min. Separate measurements over the range 245 to 290 nm showed that the absorption band of the substance causing the rise in absorbance at the end of the induction period lies very close to the CT band of the complex from which it is formed.

The principal kinetic measurements were made at 25° with *n*-hexane solutions. The absorbance was determined over recorded periods of time at 275 nm. The intensity of the incident radiation was 1.5×10^{-11} einstein $\text{ml}^{-1} \text{ sec}^{-1}$ at that wavelength. Separate tests with the principal products of the chain reaction following initiation³ (CHCl_3 , butylamine hydrochloride, butylidenebutylamine, NH_3 , and C_2Cl_6) showed that their absorbance at 275 nm was not appreciable at the concentrations formed in the solutions used.

With amine in large excess the absorbance rose rapidly to a maximum at the end of the induction period and then fell at a measurable rate to a limiting value. Plots of $\log(A_t - A_\infty)$ against time for the decay period were linear and yielded the first-order constants, k_1 , shown in Table III. The second-order constants, k_2 ,

Table III. The Rate Constants for the Decay of Absorbance with Amine in Excess (Data Are for *n*-Hexane Solutions at 25°)

[CCl_4], $M \times 10^3$	1.01	3.12	6.23	10.36	5.03	5.03	5.03
[RNH ₂], <i>M</i>	5.02	5.02	5.02	5.02	1.01	2.02	3.01
$k_1 \times 10^3$, sec^{-1}	6.8	7.7	7.2	7.5	1.4	3.0	4.1
$k_2 \times 10^3$, $M^{-1} \text{ sec}^{-1}$	1.4	1.5	1.4	1.5	1.4	1.5	1.4

were obtained by dividing the k_1 values by the amine concentration.

The formation of chloride ion in those excess-amine systems was rapid (as high as $10^{-6} M \text{ sec}^{-1}$ in the system containing 0.01036 *M* CCl_4) but could not be fitted to

any meaningful rate expression because no limiting value was approached.

With CCl_4 in large excess, the behavior was quite different. Following the induction period, rise in absorbance took place at a measurable rate and leveled off to a limiting value. Plots of $\log(A_\infty - A_t)$ against time were linear and were not appreciably affected by the CCl_4 concentration. Thus, the first-order constants with amine kept at $0.00476 M$ but with CCl_4 at 2.08, 4.15, 6.22, and $8.30 M$ were the same, $4.3 \times 10^{-4} \text{ sec}^{-1}$. Here, the induction periods were not well defined due to the slow rise in absorbance at the end of induction. The rate of formation of chloride ion was negligibly slow in these systems, being $10^{-9} M \text{ sec}^{-1}$ at the greatest (with $8.30 M \text{ CCl}_4$).

Discussion

The K_f Value. The value of the formation constant, $0.032 M^{-1}$, determined here for the complex of CCl_4 with *n*-butylamine in *n*-hexane, is so low that its accuracy is limited. The range of concentration of excess reactant used in its determination, 3.03 to $7.08 M$ amine, while lying in the proper region, *i.e.*, between 0.1 and $9.0 K_f^{-1}$, according to Person's rule,¹⁴ does not extend very far into that region due to the small magnitude of K_f . Since the pure amine is only approximately $10 M$, *i.e.*, $0.32 K_f^{-1}$, it would be impossible to meet the Person criterion much more fully.

In terms of the analysis by Deranleau,¹⁹ the range of saturation fraction, s , of the CCl_4 is only 0.088 to 0.185. For that range, the minimum relative error in K_f , $100\Delta K_f/K_f$, would be expected²⁰ to lie between ± 5.5 and $\pm 11.4\%$ for $\Delta s = 0.01$, on the assumption that the error in s is much greater than the errors in the concentrations of the amine and CCl_4 . In addition, the restriction of the saturation fraction can cause error due to molecular aggregation phenomena that may vary from one part to another of the whole range.

The earlier spectroscopic studies^{1,3,5,6} of charge-transfer interaction of aliphatic amines with haloalkanes do not provide accurate K_f values for comparison with the value obtained here. Those measurements were made over smaller ranges of saturation fraction and without concern for such criteria as those of Person¹⁴ and Deranleau¹⁹ because the interest was primarily in proof of the existence of the CT interaction and its variation with temperature rather than in the separation of $K_f\epsilon$ into K_f and ϵ . It is also unfortunate that the infrared spectroscopic²¹ and several non-spectroscopic²² studies of amine- CCl_4 and other amine-haloalkane combinations, although in agreement with the 1:1 stoichiometric model that we have used, have not yielded values of K_f .

Only the recent gas-liquid chromatographic measurements of Martire and coworkers²³ provide K_f values of

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good accuracy. They studied the 1:1 complexes of 11 different haloalkanes with two rather bulky amines, the method requiring that one of the components of the complex be nonvolatile. For di-*n*-octylmethylamine- CCl_4 they found $K_f = 0.060, 0.058, 0.056,$ and $0.054 M^{-1}$ at 30, 40, 50, and 60° , respectively, and for tri-*n*-hexylamine- CCl_4 they found $K_f = 0.026, 0.025, 0.024,$ and $0.023 M^{-1}$ at the same respective temperatures. Their results showed clearly that the K_f values depend both on steric and electronic factors. The di-*n*-octylmethylamine has the higher K_f values with CCl_4 principally because of its lower steric hindrance. In view of their results, the magnitude of the value of K_f determined here for *n*-butylamine- CCl_4 appears reasonable, since the *n*-butylamine, although a weaker donor, should show less steric hindrance to complex formation than either of the amines they employed. Martire and coworkers have also found strong evidence that, for the haloalkane-amine systems, only 1:1 acceptor-donor complexes exist at all donor concentrations up to pure donor.

Kinetics of the Photochemical Decomposition. The photochemical decomposition of the weakly bound amine- CCl_4 pair initiates a chain reaction between the amine and haloalkane. The decomposition has been written³ as follows to show the formation of the radical chain carriers in the chain initiating steps



Although a thorough kinetic study of the ensuing chain reaction has been made³ and found consistent with those initiating steps, no separate study of those first two steps has been made heretofore.

For step 1, Stevenson and Coppinger¹ and Mulliken² have noted that the $\text{RNH}_2 \cdot \text{CCl}_4$ pair, even if so weakly bonded as to constitute a contact pair, will absorb light to form an excited complex in which electron transfer is nearly complete and which may be written $(\text{RNH}_2)^+(\text{CCl}_4)^-$. This excited complex (or exciplex) would be expected to dissociate spontaneously thermally to the intimate ion pair, $\text{RNH}_2^+\text{Cl}^-$, and the trichloromethyl radical. Those suggestions would amount to writing step 1 as a two-step consecutive reaction.



The kinetic studies made here were designed to test that more detailed mechanism by use of low light intensity and low concentration of one of the reactants to slow those initiating steps and to limit the extent of ensuing chain reaction which might otherwise obscure those steps. On the assumption that the ion pair, $\text{RNH}_2^+\text{Cl}^-$, is the substance causing the rise in absorbance following the induction period, the results are in agreement with the mechanism proposed. This assumption appears reasonable in view of the finding that none of the products of the chain reaction could account for the absorbance and in view of the spectral properties of known intimate ion-pair complexes.²⁴

According to the proposed mechanism step 1a would be expected to be immediate while the rates of steps 1b and 2 should depend greatly upon which of the reactants, amine or CCl_4 , is in large excess. Our findings bear

(24) See ref 18, Chapter 13.

this out and, on the basis of the assumption made, give estimates of the rate constants for steps 1b and 2 for both cases of excess reagent.

With amine in large excess, both the formation of the ion pair, $\text{RNH}_2^+\text{Cl}^-$, by step 1b at the end of the induction period, and the decomposition of that substance by step 2, are more rapid than in the systems containing excess CCl_4 . The more rapid formation of the ion pair in the amine-rich solutions would be predicted by the greater polarity of these solutions²⁴ and the greater rate of step 2 by the large concentration of free amine. On the other hand, the CCl_4 -rich solutions contain very low concentrations of free amine, so that the ion pair, although formed more slowly, will also decompose only slowly in those solutions. Thus, the average value of the second-order velocity constants given in Table III, $1.45 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$, can be taken as the rate constant for step 2 in the amine-rich media. Similarly, the rate constant for step 1b in the CCl_4 -rich systems can be taken as the value, $4.3 \times 10^{-4} \text{ sec}^{-1}$, found at all CCl_4 concentrations for those systems.

The value of the induction time can be used to obtain a rough estimate of the rate constant of step 1b in the amine-rich solutions. Assuming that the excited par-

ticles, $(\text{RNH}_2)^+(\text{CCl}_4)^-$, formed in step 1a are forming without appreciable decomposition during the induction period and that they reach a steady state concentration by the end of that period, it can be shown that the rate constant for step 1b is equal to the reciprocal of that induction time. In that way, the induction time of 16 min observed for the amine-rich solutions corresponds to a rate constant of $1 \times 10^{-3} \text{ sec}^{-1}$ for formation of the ion pair.

The rates of Cl^- ion formation are also consistent with the proposed mechanism. With amine in large excess, the rate is high as expected from the high rate of step 2, but the high rate of step 2 also causes sufficient chain reaction to produce additional Cl^- ion, which accounts for the lack of a limiting value. With the CCl_4 in excess, step 2 is extremely slow as is also the Cl^- formation.

Acknowledgment. This research was supported in part by the Advanced Research Projects Agency, by the National Science Foundation, and by a National Defense Education Act Title IV Research Fellowship (awarded to C. J. B.). We are also indebted to J. P. Birk and J. Gasiewski for technical aid and helpful discussions.

Photodecomposition of Gas-Phase Transition Metal Carbonyl Anions

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Abstract: Photodisappearance spectra have been obtained by ion cyclotron resonance technique for ten transition metal carbonyl anions. The ion disappearance mechanism is believed to be photodissociation, although electron photodetachment was not ruled out. The spectra are interpreted on the assumption that the photodisappearance curves reflect optical absorption peaks of the gas-phase ions. Comparison of the spectra indicates that the optical absorption of the species $\text{M}(\text{CO})_n^-$ shifts in regular fashion toward the blue either on increasing n or on moving to a metal of higher atomic number. The only exceptional case, $\text{Ni}(\text{CO})_5^-$, is predicted to be anomalous by theory. Arguments are presented for assigning the optical transition involved as arising from a charge transfer process carrying a metal 3d-type electron into a higher ligand orbital. The results for $\text{Co}(\text{CO})_4^-$ are compared with solution properties of the ion and are found to be entirely consistent.

Photodisappearance investigation of gas-phase ions using trapped-ion techniques and ion cyclotron resonance (icr) detection of ion disappearance has been a successful approach to obtaining optical absorption information about a number of ionic species.²⁻⁷ The optical properties of gas-phase transition metal containing ions are of particular interest for comparison

with the large body of spectroscopic knowledge about condensed-phase transition metal species. Early investigation showed that several transition metal carbonyl anions in the gas phase have observable photodisappearance rates, and the photodisappearance rates were observed to be strongly wavelength dependent.⁸ Recent careful investigation by Richardson and Brauman⁹ of the $\text{Fe}(\text{CO})_4^-$ system yielded convincing evidence that the photodisappearance process in this case is photodissociation, rather than electron photodetachment; in agreement with earlier work,⁸ a weak peak was observed near 700 nm, and a much more intense region of photodissociation commencing near 500 nm.

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