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Kinetics of the Decomposition of Iodine Amine in Liquid Ammonia

R. KERBACHI, R. MINKWITZ*

Universitat Dortmund, Abteilung Chemie,
D-4600 Dortmund, F.R.G.

and U. ENGELHARDT

Freie Universitat, Institut fur Anorganische und Analytische Chemie, 1000 Berlin (West), F.R.G.

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Nitrogen triiodide-1-ammonia is only slightly soluble in liquid ammonia and slow decomposition is observed in this solvent, yielding ammonium iodide and nitrogen [1]. According to Jander [2–4] this decomposition reaction can be attributed to monoiodine amine forming in solution from nitrogen triiodide and ammonia in an equilibrium reaction, and decomposing to above mentioned end-products (eqn. 1)

$$3NH_2J \cdot xNH_3 \xrightarrow{\text{liquid } NH_3} 3NH_4J + N_2 + (x-2)NH_3 \qquad (1)$$

In an earlier paper we reported UV/VIS investigations of these solutions in liquid ammonia which showed the existence of an unstable compound having absorption bands at 270 and 310 nm. The intensities of both absorption bands decrease with time and another band at 254 nm, assigned to ammonium iodide, increases simultaneously.

From comparisons of chemical and spectroscopical properties of this compound with those of other known halogen amines or substituted halogen amines, we concluded that the species present in liquid ammonia is indeed monoiodine amine [5]. We now report further investigations on reaction rates at different temperatures of the decomposition reaction of iodine amine in dilute solutions in liquid ammonia.

Experimental

Solid nitrogen triiodide-3-ammonia was prepared by reaction of iodine with liquid ammonia and was purified from the simultaneously formed ammonium iodide by washing with ammonia. Pure liquid ammonia is condensed on the pure solid, and the solution thus formed was transferred to a low temperature UV-cell by means of a pre-cooled pipette. Measurements were made with a Beckman spectrometer Akta MV II. The ratios of the extinctions at t and t_0 at 310 nm were plotted in a logarithmical scale against time t. The reaction rate constants were then determined from the slope of the best straight line obtained applying the method of least squares.

Results and Discussion

Constant half-life periods at constant temperature show the reaction to be first order in rate, according to eqn. 2. Rate constants at different temperatures are given in Table I together with estimated standard deviations. An activation energy $E_A = 60 \pm 2$ kJ mol^{-1} and a frequency factor $A = 1.50\ 10^8\ s^{-1}$ can be evaluated using the Arrhenius equation (Table I, footnote b). Equation 3 gives $\Delta S^* = 86 \pm 9$ J K^{-1} mol^{-1}.

$$-\frac{dNH_2I}{dt} = k[NH_2I]\ [mol \cdot l^{-1} \cdot s^{-1}] \qquad (2)$$

$$k = 2.08 \cdot 10^{10} \cdot T \cdot e \left(\frac{\Delta S^*}{R} - \frac{E_A}{RT}\right)\ [s^{-1}] \qquad (3)$$

Calculated rate constants and half-life periods using these values are in good agreement with the experimental results (Table I).

The data show that iodine amine decomposes rather slowly below −60 °C in liquid ammonia: $t_{(1/2)c} = 664$ h, or about one month for this temperature. At −37 °C the half-life period is about one day and the reaction is about three times faster than at −45 °C and about six times faster than at −50 °C. Compared with the other halogen amines, iodine amine is the most stable compound in dilute liquid ammonia solutions. Whereas monofluorine amine is unknown (because of instability), monochloramine and monobromamine can be prepared as liquid ammonia solutions. Their decomposition rates are much higher than that of monoiodine amine. At −70 °C monochloramine decomposes almost quantitatively within 48 h [6]. Half-life periods of monobromamine are 9.5 h at −70 °C and 0.5 h at −50 °C [7]. Since it is assumed that halogen amines decompose in liquid ammonia via hydrazine as an intermediate with the formed hydrazine being oxidized by excess halogen amine [3, 4, 6], the hydrazine formation most probably is the rate determining reaction step (4).

$$H_3N\!: + NH_2{-}X \rightarrow [H_3N{-}NH_2]^+ + X^- \qquad (4)$$

This nucleophilic substitution of halogen by ammonia should conceivably be less favoured in the case of the more electropositive halogen. Adduct formation of iodine amine with solvent ammonia may add to the stabilization of this molecule. A charge transfer band attributed to such an adduct is observed in the low

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*Author to whom all correspondence should be addressed.

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TABLE I. Kinetic Data of the Decomposition Reaction of Iodine Amine in Liquid Ammonia.

Temperature	[°C] [K]	–37 236	–40 233	–45 228
First order rate constant k [s^{-1}]^a		$7.22\ 10^{-6}$ $\pm 0.17\ 10^{-6}$	$5.32\ 10^{-6}$ $\pm 0.06\ 10^{-6}$	$2.65\ 10^{-6}$ $\pm 0.04\ 10^{-6}$
Half-life period $t_{(1/2)}$ [h]^a		26.7 ± 0.6	36.2 ± 0.4	72.6 ± 1.1
Calculated rate constant k_c [s^{-1}]^b		$7.79\ 10^{-6}$ $\pm 0.23\ 10^{-6}$	$5.23\ 10^{-6}$ $\pm 0.09\ 10^{-6}$	$2.66\ 10^{-6}$ $\pm 0.03\ 10^{-6}$
Calculated half-life period $t_{(1/2)c}$ [h]^b		24.7 ± 0.7	36.8 ± 0.6	72.5 ± 0.6

[a] From slope of best straight line through experimental values (Fig 1); errors given account for statistical errors only. [b] Using the Arrhenius equation $\ln(k_c) = \ln(A) - E_A/R \cdot T$ and $E_A = 60 \pm 2$ kJ mol^{-1} and $A = 1.50\ 10^8\ s^{-1}$ (values obtained by least squares method from weighted k-values; weights taken as $w_i = 1/(\sigma_i^2 \cdot \sum_i (1/\sigma_i^2))$; errors given account for error in E_A).

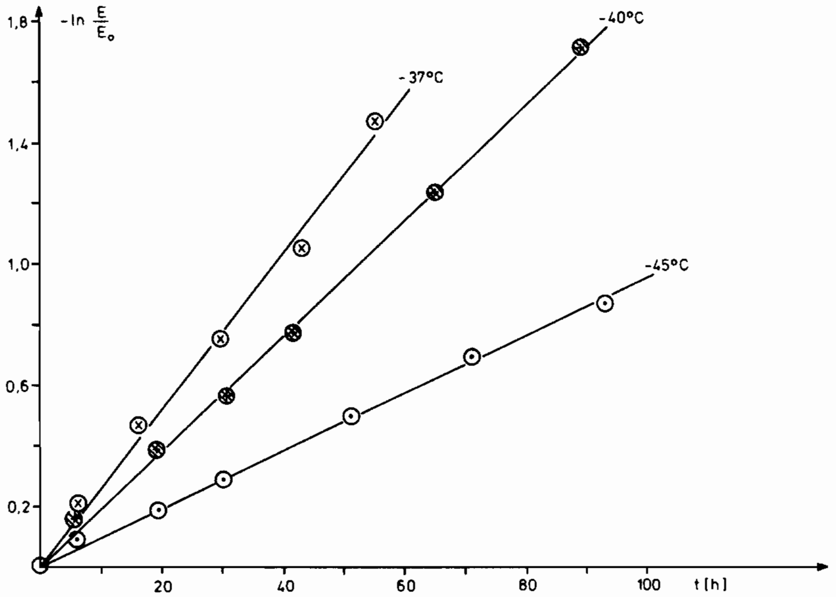

Fig. 1. Plot of $-\ln(E/E_0)$ against time of solutions of iodine amine in liquid ammonia at different temperatures. Extinctions are measured at 310 nm. Straight lines are best fits (equation of straight line $y = m \cdot x$, $\sum_i (y_i - mx_i)^2$ a minimum).

temperature spectra in liquid ammonia solutions [5]. A similar stabilization by adduct ammonia of nitrogen triiodine is well known.

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