# Photochemistry and Free-Radical Reactions in Formamide Vapour*

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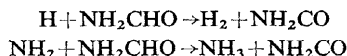
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The photolysis of formamide vapour has been studied at temperatures from 115 to 400°C and pressures from 8 to 50 torr, with 206.2 nm radiation. Products detected were CO, H_2 and NH_3, with quantum yields at 150°C of 0.8, 0.6 and 0.2 respectively. From experiments with added ethylene and with NH_2CDO and ND_2CHO, it was deduced that there were three major primary processes:

$$NH_2CHO + h\nu \rightarrow NH_2 + CO + H \ (\phi = 0.35)$$
$$\rightarrow H + NHCHO \ (\phi = 0.22)$$
$$\rightarrow NH_3 + CO \ (\phi = 0.45),$$
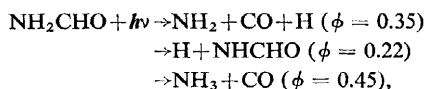
followed by the reactions,

$$H + NH_2CHO \rightarrow H_2 + NH_2CO$$
$$NH_2 + NH_2CHO \rightarrow NH_3 + NH_2CO$$

The reactions of CH_3 with NH_2CHO, ND_2CHO and NH_2CDO were also studied, and approximate Arrhenius parameters were obtained. For the first two compounds, $A = 4 \times 10^7$ (M s)$^{-1}$ and $E = 7$ kcal/mol, and for the last, $A = 2 \times 10^7$ and $E = 8$. Hydrogen was abstracted almost exclusively from the formyl position, and the deuterium isotope effect was about 6.

Below 200°C, NH_2CO radicals were thermally stable, but at higher temperatures they decomposed,

$$NH_2CO \rightarrow NH_2 + CO,$$
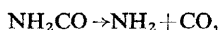
leading to a chain reaction. Approximate Arrhenius parameters of $A = 4 \times 10^9$ s^{-1} and $E = 20$ kcal were estimated for this decomposition, which was found to be pressure dependent; limiting high-pressure values of A and E will be considerably higher.

The photolysis of formamide vapour has apparently not been studied before. Some liquid-phase experiments have been reported,[1-3] but these involved sensitized rather than direct photolysis; abstraction of H from the formamide by excited species or free radicals formed from the sensitizer appeared to occur. The photolysis of formamide vapour is of interest in itself, and by analogy with acetaldehyde is a possible source of NH_2 and NH_2CO radicals. The present investigation is part of a study in this laboratory of the photochemistry and free-radical reactions of simple nitrogen compounds in the gas phase.

EXPERIMENTAL

APPARATUS

Photolyses were carried out in a conventional cylindrical quartz vessel, 100 mm long and 50 mm diam., fitted with plane Suprasil windows, and mounted in an air thermostat which could be maintained at temperatures up to 200°C. The vessel was encased in a tubular aluminium furnace which minimized temperature gradients and could be heated to 400°C. Also, within the air thermostat were Pyrex stopcocks (lubricated with silicone grease) leading to an external vacuum line, to a heated quartz-spiral pressure gauge via a heated line, and to a reservoir of liquid formamide. The latter was mounted in a metal

block normally cooled by tap-water to minimize decomposition during storage, but which could be heated to provide the desired vapour pressure of formamide.

LIGHT SOURCES

An iodine resonance lamp, described elsewhere [4] which provided virtually mono-chromatic light of 206.2 nm, was used for the photolysis of formamide. The light transmitted by the photolysis vessel was measured by a photocell with a platinum cathode sensitive only to wavelengths below about 220 nm.[4] A medium-pressure mercury arc (Hanovia S-500) was used with a Pyrex filter to photolyze selectively azomethane in the presence of formamide.

ANALYSIS

Gases non-condensable at $-196°C$ (CO, H_2, N_2 and CH_4) were removed by a Toepler pump, measured in a gas burette, and analyzed by gas chromatography or by combustion over copper oxide. Product fractions volatile at -160, -78 and $-10°C$ were analyzed by gas chromatography using a variety of columns. Ammonia was estimated quantitatively by analysis on a 2 m Poropak Q column, coated with 10 % diethanolamine, at 60° in a metal-free apparatus, using a trace of ammonia in the carrier gas to minimize peak tailing.

MATERIALS

Formamide was obtained from British Drug Houses (Canada) Ltd., and purified by trap-to-trap distillation under vacuum and prolonged degassing at 50°C. Some samples were stored over anhydrous sodium sulphate but this was later omitted as it did not appear to affect the product yields. Isotopically substituted formamides, ND_2CHO and NH_2CDO, were obtained from Merck, Sharp and Dohme of Canada Ltd., as was azomethane. Ethylene and propane were Phillips Research-grade gases.

RESULTS

LOW-TEMPERATURE PHOTOLYSIS

The major products were CO, H_2 and NH_3. Quantum yields of these were measured, using the photolysis of azomethane at 20°C as an actinometer, assuming $\phi(N_2)$ to be unity.[4] A small correction (~ 8 %) was necessary for photolysis of azomethane by light from the iodine lamp of wavelengths longer than 220 nm (transmitted by a Corning 7910 filter) which did not photolyze formamide. The quantum yields of CO and NH_3 were also corrected for a dark reaction giving these products at a rate approximately proportional to the pressure of formamide, the

TABLE 1.—QUANTUM YIELDS FROM THE PHOTOLYSIS OF FORMAMIDE

temp. (°C)	formamide pressure (torr)	$\Phi(CO)$	$\Phi(H_2)$	$\Phi(NH_3)$
115	15.9	0.74	0.54	0.13
150	8.5-49.2	0.80	0.60	0.20
185	18.2	0.91	0.79	0.14

correction being 1-15 % for CO and 50-70 % for NH_3. The dark production of NH_3 was greater than that of CO and variable, and the quantum yields are therefore less reliable. Photolyses at temperatures higher than about 130°C slowly formed a deposit on the vessel windows which reduced their transmission and affected the quantum yield measurements. Absolute yields were therefore obtained in experiments immediately before and after actinometry experiments, or later by baking the cell at 400°C between runs, which removed the deposit.

The data at 115 and 150°C represent averages of a number of experiments, while only a single experiment was done at 185°. An approximate uncertainty of ± 0.05

may be attached to the quantum yields shown in table 1. No dependence on pressure was observed in the experiments at 150°C and all yields were apparently independent of conversion, which was limited to 4 % or less.

The only other products detected were a small amount of nitrogen (between 0.3 and 0.5 % of the CO), and, in one run taken to 35 % conversion using the unfiltered mercury arc, HCN was observed, about 10 % of the CO yield. A search for HCN in typical runs at 115°C (conversion ∼4 %) was unsuccessful, and it was estimated that its yield must have been less than 0.2 % of that of CO.

The photolysis was also carried out in the presence of varying pressures of ethylene; results for a formamide pressure of 16.3 torr at 150°C are shown in fig. 1. The efficient suppression of the hydrogen yield strongly suggests that hydrogen atoms are involved in its production. About 4 % of the original yield of H_2 persisted at high pressures of ethylene, and perhaps represents a molecular photodissociation. The yield of CO is practically unaffected by up to 65 torr of ethylene. Additional products observed in the presence of ethylene were butane, propane and methane, indicative of ethyl and methyl radicals presumably formed from the reactions of hydrogen atoms with ethylene and ethyl radicals respectively. Ethane should also have been formed, but was obscured by ethylene in the chromatogram.
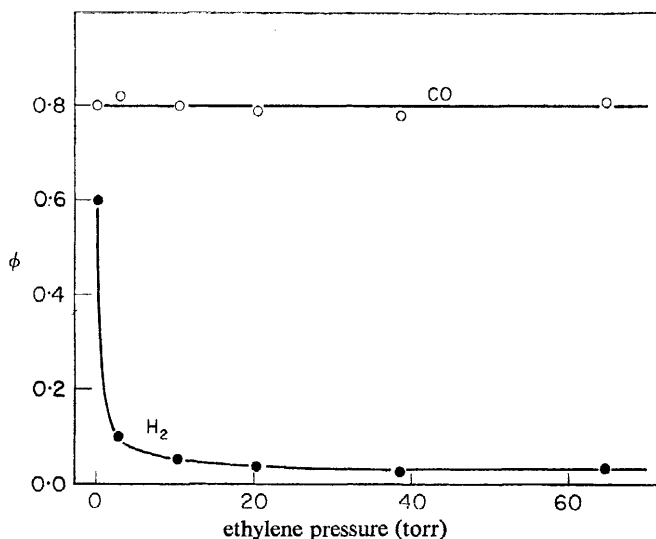

FIG. 1.—The effect of added ethylene on the quantum yields of CO and H_2 from the photolysis of formamide at 150°C.

A reciprocal plot of the data in fig. 1, after subtracting the 4 % " molecular " hydrogen, yielded a straight line from the slope of which it was estimated that at 150°C, the rate of addition of H to ethylene was about 34 times faster than the rate of abstraction from formamide.

To determine whether the hydrogen atoms produced in the photolysis originated from the formyl or the amino group, ND_2CHO and NH_2CDO were photolyzed alone and in the presence of high pressures of propane. The isotopic composition of the resulting hydrogen is shown in table 2.

Several conclusions may be drawn from these data. The lack of dependence of the % H_2 and HD on propane pressure in the ND_2CHO photolysis, and the lack of D_2 in the NH_2CDO system, indicate that virtually all the H atoms reacted with propane. The lack of D_2 from ND_2CHO shows that the residual hydrogen evident

in fig. 1, if it does come from a molecular photodissociation, must consist of one hydrogen atom from each position. A correction to the data in table 2 for this extra HD will be roughly balanced by a correction for the estimated 2 % H impurity in the deuteriated formamides, so that the data as they stand should approximately reflect the primary yields of H and D atoms. Hydrogen atoms clearly come from

TABLE 2.—ISOTOPIC COMPOSITION OF HYDROGEN FROM PHOTOLYSIS OF ND_2CHO AND NH_2CDO WITH AND WITHOUT PROPANE PRESENT. FORMAMIDE PRESSURE ABOUT 22 torr, TEMPERATURE 150°C.

	propane pressure (torr)	H_2 (%)	HD (%)	D_2 (%)	Φ of total
ND_2CHO	0.0	60.0	40.0	<0.5	0.59
	242.4	63.9	36.1	<0.5	0.61
	473.4	63.5	36.5	<0.5	0.57
NH_2CDO	0.0	9.7	52.2	38.1	0.44
	500.4	41.3	58.7	<0.5	0.45

both positions, with 64 and 59 % coming from the formyl position in ND_2CHO and NH_2CDO respectively. There is thus a small deuterium isotope effect in the primary process, favouring dissociation of H. There is also an appreciable isotope effect in the total quantum yield of hydrogen (table 2). The results with the deuterated formamides alone show that, as with CH_3, abstraction by hydrogen atoms is almost exclusively at the formyl position ; a large deuterium isotope effect is also apparent.

REACTION OF METHYL RADICALS WITH FORMAMIDE

This reaction was studied briefly in order to obtain information both about the relative rates of abstraction of H from the two positions in formamide, and about the subsequent behaviour of the resulting NH_2CO and $NHCHO$ radicals. Methyl radicals were produced by the photolysis of azomethane. Rates of formation of methane and ethane are given in table 3, together with overall rate constants for abstraction from formamide calculated in the usual way, assuming $[CH_3] = (R_{C_2H_6}/k)^{\frac{1}{2}}$, using Shepp's value [5] of $k = 2.2 \times 10^{10}$ (Ms)$^{-1}$. The correction for methane arising by abstraction from azomethane was made from data obtained in the absence of formamide (not shown).

From the data in table 3, the overall rate constants for abstraction of hydrogen or deuterium from the 3 formamides can be represented by the expressions,

$$k_{NH_2CHO} \approx k_{ND_2CHO} \approx 4(\pm 1) \times 10^7 \exp\left(-7000(\pm 2000)/RT\right) \quad (M\ s)^{-1} ;$$

$$k_{NH_2CDO} \approx 2(\pm 1) \times 10^7 \exp\left(-8000(\pm 2000)/RT\right) \quad (Ms)^{-1}.$$

The values for NH_2CHO and ND_2CHO are consistent, within the experimental error, with the more extensive and accurate data reported by Cafferata et al.[6] and by Gray and Leyshon,[7] while the yields of CH_3D from the deuterated formamides show that abstraction of the formyl hydrogen is strongly preferred. An inconsistency is evident in the latter data, however, which suggests that not all of the methane was produced by abstraction from formamide or azomethane, as was assumed. The yield of CH_3D indicates that 79 (± 5) % of the abstraction from NH_2CDO was from the formyl position. The deuterium isotope effect, which must be at least as large as the ratio of the overall rate constants, k_{ND_2CHO}/k_{NH_2CDO}, which was 6.1 (± 0.3), should then have led to a negligible yield of CH_3D from ND_2CHO; this was not the case (table 3). Various tests and experiments were performed, which

appear to rule out abstraction of D from a reaction product, or from polymer on the wall, or isotopic exchange, as sources of the extra CH_3D, and it was concluded that the most probable source was the disproportionation reaction,

$$CH_3 + ND_2CO \rightarrow CH_3D + DNCO. \qquad (1)$$

If the corresponding reaction occurred to the same extent in the NH_2CDO system, yielding CH_4, the percentage abstraction from the formyl position should be adjusted upwards to a value of 97 (± 10) %. It thus appears probable that more than 90 % of the abstraction by CH_3 from NH_2CDO, and essentially all the abstraction from ND_2CHO and NH_2CHO was from the formyl position. It follows that k_H/k_D for the latter pair is about 6, which lies within the normal range for primary deuterium isotope effects in abstraction reactions.

TABLE 3.—REACTION OF METHYL RADICALS WITH FORMAMIDE

	temp. °C	azomethane	formamide	R_{CH_4}	$R_{C_2H_6}$	k	CH_3D*	$CH_3D\dagger$
		$M \times 10^4$		$M/s \times 10^9$		$(M/s)^{-1} \times 10^{-4}$	%	%
NH_2CHO	144.4	0.97	5.86	1.72	1.21	0.96	—	—
	165.8	1.84	14.1	6.89	1.24	1.7	—	—
	184.3	1.78	13.1	3.01	0.17	2.1	—	—
ND_2CHO	144.3	0.96	4.55	1.66	1.85	0.88	11	16
	145.9	1.03	4.45	1.85	1.92	0.99	—	—
	164.8	0.92	4.40	2.22	1.46	1.4	12	17
	167.9	1.82	6.53	1.92	0.49	1.2	11	17
	183.0	0.89	3.66	2.34	0.93	2.0	14	21
	183.8	0.70	4.30	2.05	0.59	2.1	13	18
NH_2CDO	144.2	0.97	9.00	1.07	2.60	0.15	33	75
	146.4	0.77	11.0	0.75	1.15	0.17	50	85
	165.0	0.94	7.42	1.73	2.96	0.21	38	74
	165.2	0.48	15.8	1.22	1.19	0.25	56	79
	183.0	0.67	14.5	1.17	0.40	0.45	—	—
	183.7	0.90	5.66	1.59	1.77	0.27	27	84

* : % of total methane ; † : % of methane from formamide.

In their study of the reaction of CH_3 with NH_2CHO and ND_2CHO (which appeared when the present paper was almost ready for submission), Gray and Leyshon [7] reached conclusions similar to ours regarding both the preferential abstraction of the formyl hydrogen and the occurrence of reaction (1). Because our data, although fewer and thus less accurate than those of Gray and Leyshon, include measurements with NH_2CDO as well as with ND_2CHO and NH_2CHO, they show even more clearly that extra methane containing amide hydrogen must have been formed by some secondary process such as reaction (1). Spall and Steacie [8] postulated the occurrence of reaction (1) for similar reasons, viz., to account for the production of extra methane in the photolysis of acetamide.

An attempt was made to detect acetamide, which might be expected from the combination reaction corresponding to reaction (1). None was found, using a 0.3 m Poropak Q column at 135°C, and it was estimated that acetamide must have been less than 5 % of the CH_4 yield. The HNCO expected from reaction (1) was also not detected, but it reacts with ammonia to form a non-volatile product.[4] Gray and Leyshon [7] did in fact detect some HNCO in their experiments. No other products from subsequent reactions of NH_2CO radicals were detected in the $CH_3 + NH_2CHO$ system. Yields of CO and NH_3 were close to those expected from the dark reaction. Additional CO was less than 2 % of the CH_4 yield, and an upper

limit for HCN (also a possible product) was about 1 %. Yields of NH_3 were more uncertain because of the larger dark reaction.

HIGH-TEMPERATURE PHOTOLYSIS (200-400°C)

At temperatures above 200°C, production of CO and NH_3 began to rise sharply. Quantum yields of CO, H_2 and NH_3 in this temperature range are plotted in Arrhenius form, together with the low temperature data, in fig. 2. The absorbed light intensity ($\sim 1.4 \times 10^{-9}$ einsteins $l.^{-1}$ s^{-1}) and the concentration of formamide ($\sim 6 \times 10^{-4}$ M) were held approximately constant. At the higher temperatures, a dark reaction formed H_2 as well as CO and NH_3; this rose from 7 % of the total H_2 at 242°C to 90 % at 387°C, making estimation of $\Phi(H_2)$ unreliable. Fig. 2 shows that CO and NH_3, but not H_2, are formed in a chain reaction. The apparent activation energy of CO formation, after subtraction of the small non-chain yield estimated by extrapolation of the low-temperature data, is 20 (± 1) kcal/mol.
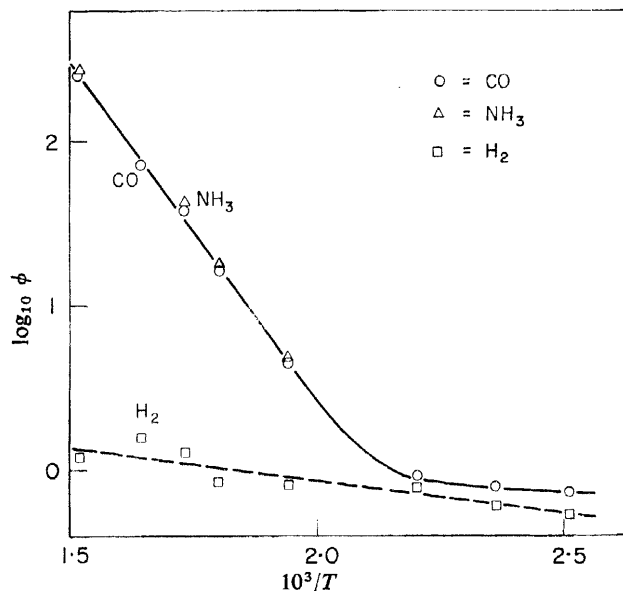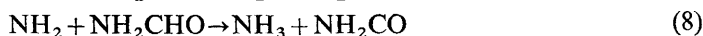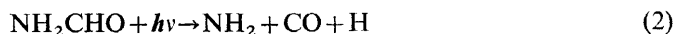

FIG. 2.—Arrhenius plot of the quantum yields of CO, H_2 and NH_3 from the photolysis of formamide.

DISCUSSION

MECHANISM OF THE LOW-TEMPERATURE PHOTOLYSIS

The following primary processes and secondary reactions are probably involved in the photolysis below 200°C:

$$NH_2CHO + h\nu \rightarrow NH_2 + CO + H \tag{2}$$

$$\rightarrow NH_2CO + H \tag{3}$$

$$\rightarrow NHCHO + H \tag{4}$$

$$\rightarrow NH_3 + CO \tag{5}$$

$$\rightarrow H_2 + HNCO \tag{6}$$

$$H + NH_2CHO \rightarrow H_2 + NH_2CO \tag{7}$$

$$NH_2 + NH_2CHO \rightarrow NH_3 + NH_2CO \tag{8}$$

The experiments with methyl radicals showed that NH_2CO radicals must disappear in reactions that produce no CO, no H_2 and probably no NH_3. This conclusion is supported by the non-chain character of the photolysis below 200°C, which shows clearly that the NH_2CO radicals were not decomposing thermally. It is probable that NHCHO radicals formed in reaction (4) similarly do not contribute to the observed reaction products (they may, in fact, be converted to NH_2CO by metathesis with formamide). If follows therefore that reactions (2)-(8) must account for all the CO, H_2 and NH_3 observed.

Primary processes (2) and (3) are suggested by analogy with the photolysis of acetaldehyde, and to account for the production of CO and formyl H atoms. Reaction (2) may involve initial formation of HCO, followed by its decomposition to H + CO. Reaction (4) is postulated because the data in table 2 show that H atoms from the amino group were produced in the photolysis. Reaction (5) is a source of CO unaccompanied by H_2, which is required because $\Phi(CO) > \Phi(H_2)$. Reaction (6) accounts for the small residual yield of H_2 in the presence of ethylene. The abstraction reactions, (7) and (8), undoubtedly occur. The results of the photolysis of the deuterated formamides with and without propane (table 2) provide clear evidence for reaction (7), while the reaction of NH_2 with formamide should have a rate comparable to that of CH_3 radicals. We can reject an alternative course for reaction (7), suggested by Jamieson,[9] yielding $H_2 + HCN + OH$, because HCN was not observed. The lack of dependence of $\Phi(H_2)$ and $\Phi(NH_3)$ on formamide pressure at 150°C indicates that virtually all the H atoms and NH_2 radicals reacted with formamide.

Quantum yields at 150°C for the 5 suggested primary processes may now be estimated. Reaction (6) is most easily dealt with, since from fig. 1, $\Phi_6 = 0.03$; this should be regarded as an upper limit because the residual H_2 might have come from another source (abstraction from ethylene by translationally hot H, for example). The extent of reaction (4) may also be simply estimated from the data in table 2, taking an average yield of amino H for the two deuterated formamides, which gives $\Phi_4 = 0.22$. For the remaining 3 primary processes, the two relations, $\Phi_2 + \Phi_3 = \Phi(H_2) - \Phi_4 - \Phi_6 = 0.35$, and $\Phi_2 + \Phi_5 = \Phi(CO) = 0.80$, must hold. These relations can be satisfied between the two limiting conditions, $\Phi_2 = 0$, and $\Phi_3 = 0$, which lead to values of 0, 0.35 and 0.80, and 0.35, 0, and 0.45, for Φ_2, Φ_3, and Φ_5 respectively. These in turn lead to values of 1.40 and 1.05 for the sum of the quantum yields of the 5 primary processes. The requirement that this sum should not exceed unity suggests that Φ_3 is, in fact, close to zero. Thus, the best estimates for the quantum yields of the 5 primary processes are $\Phi_2 = 0.35$, $\Phi_3 = 0$, $\Phi_4 = 0.22$, $\Phi_5 = 0.45$ and $\Phi_6 = 0.03$.

The foregoing estimate of primary quantum yields was based on yields of CO and H_2, with no consideration of the NH_3 production. The proposed mechanism predicts that $\Phi(NH_3)$ should equal $\Phi(CO)$, whereas it was much less. Despite a large correction for the dark reaction, the considerable uncertainty in the NH_3 yields cannot account for such a large discrepancy. The most probable cause of the NH_3 deficit would appear to be the disproportionation reaction,

$$2\ NH_2CO \rightarrow HNCO + NH_2CHO \qquad (9)$$

followed by reaction of HNCO with NH_3 to give non-volatile products.[4] The NH_3 deficit was about half the predicted yield of NH_2CO radicals, so that reaction (9) would have had to be almost quantitative to account for it. Loss of some NH_2 radicals by combination with NH_2CO could have caused part of the deficit.

Little can be said about the excited state or states of formamide which are precursors to reactions (2)-(6). There is no evidence for collisional de-excitation of

such precursors, which therefore must dissociate rapidly. The 206.2 nm radiation used in the photolysis lies far out on the long-wavelength tail of the first absorption band of formamide; a consequence of this was a sharp dependence on temperature of the molar extinction coefficient, which increased from 42 at 117°C to 82 at 387°C. The first absorption band of formamide ($\lambda_{max} = 117$ nm) has been attributed to a $\pi \rightarrow \pi^*$ transition,[10] but probably represents several overlapping transitions; the occurrence of three different major modes of photodissociation certainly suggests this. Thus, reaction (2) is typical of a carbonyl compound; reaction (4) is characteristic of the NH_2 chromophore, while reaction (5) involves the whole molecule.

PHOTOLYSIS MECHANISM AT HIGH TEMPERATURE (200-400°C)

There seems little doubt that the sharp increase in CO and NH_3 production at these temperatures was due to the chain sequence,

$$NH_2CO \rightarrow CO + NH_2 \qquad (10)$$

$$NH_2 + NH_2CHO \rightarrow NH_3 + NH_2CO \qquad (11)$$
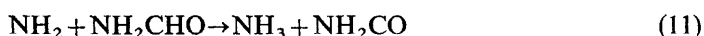
The observed activation energy for the chain of 20 kcal/mol is much too high for reaction (11), for which a value similar to that for abstraction by CH_3 might be expected.[6] Reaction (10) is thus probably rate-controlling, and NH_2CO the predominant radical present, with chain termination occurring by its combination or disproportionation reactions. If the activation energy of 20 kcal may be ascribed to reaction (10), and the rate of combination of NH_2CO radicals is equal to that for CH_3, a frequency factor of 4×10^9 s^{-1} may be estimated. By analogy with the CH_3CO radical,[11, 12] it seemed likely that reaction (10) might be pressure-dependent and preliminary experiments have confirmed this; a detailed study of the pressure-dependence is now in progress.[13] The high-pressure values of E and A will be considerably higher than those obtained from fig. 2. High-pressure values of $A = 10^{10.3}$ and $E = 15$ have been reported for the acetyl radical,[9] and it seems clear that NH_2CO is notably more stable than CH_3CO, as had been suggested by Spall and Steacie.[8] From a study of the photolysis of acetamide, these authors estimated that E_{10} was 29 kcal/mol, but this was based on an estimate of $k_{10} = 21$ at 530 K and the assumption that $A_{10} = 10^{13}$ s^{-1}. The present results give $k_{10} = 25$ at 530 K, in close agreement. The alternative decomposition of NH_2CO to $HNCO + H$, which has been proposed, did not occur even at 400°C in the present system.

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