The Photolysis of Acetaldehyde. Part III. The Reaction in the Presence of Nitric Oxide.*

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The photolysis of acetaldehyde at high temperatures (250—300°) in the presence of nitric oxide has been studied, chiefly by mass-spectrometric analysis of the products of the reaction. The rates of consumption of aldehyde and nitric oxide are approximately equal. Ethane is not a product of the inhibited reaction. Reactions of nitric oxide with the CHO radical (or with hydrogen atoms derived from it) either do not take place to any considerable extent or are followed by substantially complete regeneration of the nitric oxide. The fate of the nitric oxide is discussed. Estimates are made of the relative contributions of radical production and molecular rearrangement to the primary process at 2537 and 3130 Å.

The photolysis of acetaldehyde at temperatures in the region 250—300° is strongly inhibited by small amounts of nitric oxide. Mitchell and Hinshelwood (*Proc. Roy. Soc.*, 1937, **159**, 32) found that a few units % of nitric oxide reduced the quantum efficiency from large values to unity. Estimates of the overall collision efficiency for the reaction of nitric oxide with alkyl radicals have been made (Forsyth, *Trans. Faraday Soc.*, 1941, **37**, 312; Durham and Steacie, *J. Chem. Phys.*, 1952, **20**, 582) but the precise mechanism by which nitric oxide inhibits low-temperature reactions, and in particular the final fate of the nitric oxide itself, are by no means clear. An analytical study of the products of the photolysis of acetaldehyde in the presence of nitric oxide has therefore been made in the hope of throwing some light on this problem. The photolysis of acetaldehyde itself has been the subject of a number of recent studies and the main features of the reaction are well established. A number of obscurities remain. In particular, little is known of the part played by the CHO radicals or of the mechanism by which hydrogen is formed. Information on these points may also be obtained from a study of the photolysis in the presence of nitric oxide. Values for the relative contributions of radical production and of direct molecular rearrangement to the primary process may be derived from a knowledge of the rates of methane formation in the normal and the fully inhibited reaction.

Experimental

The experimental methods were essentially similar to those previously employed (Danby, Buchanan, and Henderson, *J.*, 1951, 1426). Two sources of radiation were used, a Thermal Syndicate low-pressure mercury lamp radiating almost entirely at 2537 Å, and a 125-w Osira mercury lamp with the outer glass envelope removed, operated in conjunction with filters to isolate the region around 3130 Å (Bowen, *J.*, 1935, 76). Both lamps were supplied from a constant-voltage transformer.

Analyses of reaction products were made with a Metropolitan-Vickers mass-spectrometer Type M.S.2, conventional techniques being used. In a number of experiments the amounts of unchanged aldehyde and nitric oxide were also determined by chemical analysis, the method of Danby and Hinshelwood (*Proc. Roy. Soc.*, 1941, *A*, **179**, 169) being used for the former, and that of Musgrave and Hinshelwood (*ibid.*, 1932, *A*, **132**, 23) for the latter. The mass-spectrometer gave results in excellent agreement with those obtained by chemical methods.

Results and Discussion

The Relative Reaction Rates of Aldehyde and Nitric Oxide.—Table 1 gives the results of analyses of the products of the photolysis of acetaldehyde in the presence of nitric oxide by radiation of wave-length 3130 Å. Similar experiments were carried out at 2537 Å. The results are summarised in Table 2, together with data for the uninhibited reaction.

The ratio of the rate of formation of methane to that of carbon monoxide, which is

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TABLE 1. *Products of photolysis of acetaldehyde in presence of nitric oxide at* 3130 Å *and* 300°.

(Initial pressures : $CH_3{\cdot}CHO$ 100 mm., NO 50 mm.)

$CH_3{\cdot}CHO$ decomposed, mm.	NO reacted, mm.	CO formed, mm.	CH_4 formed, mm.	H_2 formed, mm.	$CH_3{\cdot}CHO$ decomposed, mm.	NO reacted, mm.	CO formed, mm.	CH_4 formed, mm.	H_2 formed, mm.
3·3	3·5	3·5	0·25	0·06	4·6	4·5	4·5	0·29	0·10
4·2	4·4	4·3	0·35	0·10	6·0	6·3	6·4	0·50	0·15

TABLE 2.

$NO/CH_3{\cdot}CHO$	$CO/CH_3{\cdot}CHO$	CH_4/CO	H_2/CO	C_2H_6/CO	$NO/CH_3{\cdot}CHO$	$CO/CH_3{\cdot}CHO$	CH_4/CO	H_2/CO	C_2H_6/CO
	3130 Å, inhibited					3130 Å, uninhibited			
1·06	1·06	0·07	0·02	0	—	0·82	0·95	0·01	0·04
1·04	1·02	0·08	0·02	0	—	0·93	0·92	0·02	0·04
0·98	0·98	0·06	0·02	0	—	0·95	0·93	0·02	0·03
1·05	1·07	0·08	0·02	0	—	0·97	0·90	0·02	0·04
					—	0·96	0·90	0·02	0·04
	2537 Å, inhibited								
1·04	0·93	0·18	0·08	0					
0·99	1·07	0·19	0·08	0					
1·01	1·07	0·16	0·08	0					

(The values for aldehyde and nitric oxide represent the amounts which have *reacted* : those for products are amounts *formed*.)

practically unity for the uninhibited reaction, is reduced in the presence of nitric oxide to a small value, but not to zero. No ethane could be detected in the products of the inhibited reaction. The detection of small amounts of ethane by mass-spectrometer in gas mixtures containing nitric oxide presents special problems which have been discussed by Danby, Spall, Stubbs, and Hinshelwood (*Proc. Roy. Soc.*, 1954, *A*, **223**, 421). In a series of experiments, samples of the products of the photolysis of aldehyde in the presence of nitric oxide were treated with moist sodium hydrogen sulphite or sodium hydroxide to remove unchanged aldehyde and with moist ferrous sulphate to remove nitric oxide before admission to the mass-spectrometer. Under these conditions very small traces of ethane, if present, would have been detected. These experiments proved negative.

The following reaction mechanism adequately accounts for the main features of the acetaldehyde photolysis at elevated temperatures (Leermakers, *J. Amer. Chem. Soc.*, **1934**, **56**, 1537) :

$$CH_3{\cdot}CHO + h\nu = CH_4 + CO \tag{1}$$

$$CH_3{\cdot}CHO + h\nu = CH_3 + CHO \tag{2}$$

$$CH_3 + CH_3{\cdot}CHO = CH_4 + CO + CH_3 \tag{3}$$

$$2CH_3 = C_2H_6 \tag{4}$$

Estimates of the relative participation of reactions (1) and (2) in the primary process have been made by Gorin (*Acta Physiochim. U.R.S.S.*, 1938, **9**, 691 ; *J. Chem. Phys.*, 1938, **7**, 257) and by Blacet and Heldman (*J. Amer. Chem. Soc.*, 1942, **64**, 889, 893) from studies of the photolysis in the presence of iodine vapour. Further evidence on this point from the present work will be discussed later. Reaction (2) largely predominates, especially at longer wave-lengths. If we therefore neglect reaction (1) for the moment it follows from the equality in the rates of consumption of aldehyde and nitric oxide that either the methyl or the formyl radical from reaction (2), but not both, can react with nitric oxide to produce a stable complex. As the formation of ethane is completely suppressed by nitric oxide while that of carbon monoxide is unaffected, it is clearly the methyl radical which reacts. In the presence of nitric oxide, therefore, the reaction

$$CH_3 + NO = \text{products} \tag{5}$$

completely replaces reactions (3) and (4). If the formyl radicals interact with nitric oxide a cycle of reactions must ensue which leads to substantially complete regeneration of the nitric oxide and carbon monoxide, such as

$$CHO + NO = CHO{\cdot}NO \tag{6}$$

$$2CHO{\cdot}NO = 2CO + 2NO + H_2 \tag{7}$$

Alternatively, if the formyl radical dissociates on formation, similar considerations must apply to the hydrogen atom formed:

$$CHO = CO + H \quad (8)$$
$$H + NO = NOH \quad (9)$$
$$2NOH = 2NO + H_2 \quad (10)$$

The Fate of the Nitric Oxide.—Although an amount of nitric oxide roughly equal to that of the aldehyde decomposed undergoes reaction, only small amounts of nitrogen-containing compounds can be detected in the gaseous reaction products. The immediate addition product of a methyl radical and nitric oxide would be $CH_3{\cdot}NO$ and Raley, Rust, and Vaughan (*J. Amer. Chem. Soc.*, 1948, **70**, 88) have reported the detection of appreciable amounts of the isomer formaldoxime, $CH_2{:}N{\cdot}OH$, in the products of the thermal decomposition of di-*tert.*-butyl peroxide in the presence of nitric oxide at about 210°. Small peaks at M/e 45 are present in the mass-spectra of some of the samples of products of the aldehyde photolysis in presence of nitric oxide but they correspond to amounts of formaldoxime far too small to account for more than a fraction of the nitric oxide consumed. At much higher temperatures (630°) a large proportion of the nitric oxide interacting with alkyl radicals appears in the final products in the form of hydrogen cyanide (Danby, Spall, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1953, *A*, **218**, 430). No trace of hydrogen cyanide or ammonia could be detected by mass spectrometer or chemical tests in the products of the inhibited aldehyde photolysis at 300°. Formaldoxime is known to polymerise very readily to a solid trimer (Schall, *Ber.*, 1891, **24**, 573). The evidence therefore suggests that the interaction of methyl radicals with nitric oxide leads to the formation of formaldoxime which, at 300°, polymerises to a solid of low vapour pressure, and at higher temperatures decomposes to form hydrogen cyanide and water.

The Formation of Hydrogen.—In the uninhibited reaction the amount of hydrogen in the products is small, being almost exactly half that of the ethane (Table 2). It can be shown that this is the ratio of ethane to hydrogen which would be obtained were the hydrogen entirely formed by the reaction

$$CHO + CH_3{\cdot}CHO = H_2 + 2CO + CH_3 \quad (11)$$

Both the alternative fates for the formyl radical in the presence of nitric oxide given by (6) and (7) or by (8), (9), and (10) would lead to the formation of an amount of hydrogen in the inhibited reaction equal to half that of the carbon monoxide. The analytical results show that only a small proportion of this amount of hydrogen is actually present in the products. The close equivalence of the amounts of aldehyde decomposed and of carbon monoxide formed rules out reactions such as the formation of glyoxal. In the same way the figures for the rate of consumption of nitric oxide show that reactions such as

$$2NOH = H_2O + N_2O \quad (12)$$

cannot be taking place to a very great extent. Small amounts of water vapour, nitrogen, and nitrous oxide are, in fact, present in the reaction products but the amounts are too small to account for the large discrepancy in the amounts of hydrogen. It has, however, been observed recently that olefins such as propylene and butene are as powerful inhibitors of the exchange reaction between hydrogen and deuterium as is nitric oxide (unpublished observations, this laboratory). As formaldoxime contains a double bond, it seems probable that it may react with hydrogen atoms in a similar manner. The product of such an interaction would be a free radical which might therefore polymerise the more readily, thus providing a further reason for the absence of appreciable amounts of formaldoxime in the volatile products.

The Effect of Wave-length on the Primary Process.—The rate of reaction (1) is given by the rate of formation of methane in the inhibited reaction; that of reaction (2) by subtraction of the rate of (1) from the rate of consumption of aldehyde. We thus obtain the values for the relative probabilities of molecular rearrangement and radical formation in the primary process given in Table 3. The values obtained fall between those of Gorin and of Blacet and Heldman (*locc. cit.*) at the longer wave-length but correspond to a lower relative probability of molecular rearrangement at 2537 Å than either of those previously reported. The earlier work, however, relates to photolysis at much lower temperatures.

The results in Table 3 show that approximately 9% and 17% of the aldehyde decomposes without forming radicals at 3130 and 2537 Å, respectively. As the consumption of nitric oxide is nearly equal to that of aldehyde at both wave-lengths it follows that a small amount of nitric oxide reacts in some way other than with methyl radicals. The equivalence of the amounts of aldehyde decomposed and of carbon monoxide formed shows that a stable complex of nitric oxide and the formyl radical is not formed. The presence of small amounts of nitrous oxide and of water vapour in the products as already mentioned suggests that reactions such as (12) probably take place to a sufficient extent to account for the difference.

TABLE 3. *Contributions of molecular rearrangement and radical formation to the aldehyde primary process at* 300°.

Wave-length	$CH_4/(CO - CH_4)$			Wave-length	$CH_4/(CO - CH_4)$		
3130 Å	0·07	Mean 0·08	Molecular 9·3%	2537 Å	0·22	Mean 0·21	Molecular 17·3%
	0·09		Radical 90·7%		0·23		Radical 82·7%
	0·07				0·19		
	0·09						

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