Mass-spectrometric Investigation of the Formation of Di-imide by the Catalytic Decomposition of Hydrazine at Low Pressures on Platinum

By E. M. A. WILLHOFT
(*The Gas Council Research Group, London, S.W.*6)
and A. J. B. ROBERTSON
(*Department of Chemistry, King's College, London, W.C.*2)

WHEN anhydrous hydrazine, at pressures of 10^{-4} torr and less, was decomposed on an electrically heated platinum filament in the conventional vacuum-flow system[1] used for ammonia decomposition, two observations suggested the formation of some transient intermediate. First, with the filament at temperatures above 700°K in a glass vessel at room temperature, three molecules of hydrazine were decomposed for every molecule striking the filament. Thus, some intermediate, evaporating from the platinum, could bring about further decomposition of the hydrazine in an adsorbed layer on the walls of the vessel, or perhaps to some extent in the gas phase. Second, the ratio of hydrogen : nitrogen in the product, after these had been passed through a trap cooled in liquid air, was 2·5 : 1. This is explicable if an intermediate is formed in which the nitrogen : hydrogen ratio is greater than that in hydrazine, and which can be condensed in a liquid-air trap, or at the walls of the vessel. The need for postulating this was further emphasised because, in addition to nitrogen and hydrogen, some ammonia was formed which was condensed in the liquid-air trap.

A mass-spectrometric search was made for intermediates evaporating from a heated platinum surface. An apparatus similar to the ultrahigh-vacuum system[1] was connected to a quadrupole mass spectrometer (Centronic EAL Quad 250) so that particles could pass directly from the catalytic surface into the ionising electron beam. Hydrazine flowed continuously into a vessel, connected to a large pumping line, and to a separate glass tube leading to the continuously-pumped mass spectrometer. The vessel contained the platinum catalyst as a thin foil about 2 × 2 cm. square and 8 μm. thick, or alternatively, as a coiled filament 30 cm. long and 75 μm diameter.

In the absence of catalytic reaction, hydrazine at a pressure of 2×10^{-5} torr gave the mass spectrum shown in the Table.

TABLE

Mass spectrum of hydrazine in a quadrupole spectrometer with a nominal electron energy of 70 ev

Mass (*m/e*)	14	15	16	17	28	29	30	31	32
Relative intensity..	1	2	24	40	24	31	41	43	100

On heating the platinum filament to about 950°K masses 31 and 32 both decreased to about 62% of their previous values whereas masses 30 and 29 decreased respectively to 70% and 76% of their previous values. The peak height of mass 28 increased by a factor of about 5. No peaks appeared with mass greater than that of hydrazine. These results suggested the formation of di-imide which ionised to $N_2H_2^+$ and N_2H^+. Since the ionisation potential of di-imide would be less than the appearance potential of $N_2H_2^+$ from N_2H_4, much greater relative changes in the mass spectrum should occur at low electron energies if di-imide is formed.[2,3] With low-energy electrons large relative increases of masses 30, 29, 16, and 15 occurred when the platinum foil was heated to about 1800°K; for example, with a nominal electron energy of 7 ev these peaks could be increased by a factor of about 2, giving actual heights on the oscillographic screen of several centimetres (except for NH^+). In contrast, masses 32 and 31 decreased in harmony with each other. Mass 17 decreased also, but to a much smaller extent. The decrease of mass 17 arising from hydrazine decomposition on the platinum catalyst was offset by the simultaneous formation of ammonia. When ammonia alone was decomposed on platinum no NH_2 or NH radicals could be detected. The observations were consistent with the very low yield of NH_2 and NH radicals observed by Melton and Emmett[4] who also decomposed ammonia on platinum.

The simplest interpretation of these results is that the reactive intermediate is di-imide which was reported by Foner and Hudson[5] to be formed by decomposition of hydrazine in the gas phase (the conditions were unspecified). The synthesis of NO from residual water and hydrazine could not account for the increase in the mass 30 peak in the present experiments since the residual water pressure was too low. In any case, only negligible reaction of water was observed by direct observation of the mass 18 peak with the catalyst at room temperature and at about 950°K. The extremely small 27 peak in the spectra showed that any ethane present could not contribute appreciably to mass 30. The partial pressure of the di-imide formed can be estimated from the mass spectra at 70 ev to be 7×10^{-7} torr. It was assumed that the cross-sections are equal for ionisation of N_2H_4 to $N_2H_4^+$ and N_2N_2 to $N_2H_2^+$. For the pumping speed used the partial pressure of di-imide corresponds to a reaction probability (*i.e.*, the probability of an N_2H_4 molecule decomposing to give N_2H_2 at a collision on the heated platinum catalyst) of about 0·2. Since it is likely that reaction of N_2H_4 with N_2H_2 also occurs at the walls of the reaction vessel, the true reaction probability may well exceed 0·2 at the temperatures investigated.

If the extra contribution to peak 29 when hydrazine is decomposed arises only from dissociative ionisation of N_2H_2 to N_2H^+, the relative intensities of peaks 30 and 29 in the mass spectrum of di-imide (at 70 ev energy) are 76 and 100, respectively. Similarly at a nominal 12 ev the relative contributions of masses 30 (N_2H_2), 29 (N_2H), 16 (NH_2), and 15 (NH) to the di-imide spectrum were 100, 28, 4, and 1 respectively. Corey and Mock[6] obtained peaks at masses 28, 29, and 30 by thermal decomposition of anthracene-9,10-di-imine, and deduced that di-imide is formed. Their mass spectrum was for a nominal electron energy of 13 ev. The possibility of contributions to peaks 29, 16, and 15 from thermally formed N_2H, NH_2, and NH radicals on the platinum catalyst in the present work needs further investigation.

When oxygen was mixed with the hydrazine, heating the catalyst produced an increase of mass 30 by a factor of 4 (with a nominal electron energy of 44 ev) but there was no increase of masses 16 and 29; in fact they decreased. No NO_2 formation was observed. Clearly the oxygen was producing NO which was contributing to mass 30, the reaction proceeding with high efficiency.

(*Received, March* 13*th*, 1967; *Com.* **241.**)

A. J. B. Robertson and E. M. A. Willhoft, *Trans. Faraday Soc.*, 1967, **63**, 476.
[2] A. J. B. Robertson, *Discuss. Faraday Soc.*, 1953, **14**, 115.
[3] A. J. B. Robertson in "Mass Spectrometry" Institute of Petroleum, London, 1952, p. 47.
[4] C. E. Melton and P. H. Emmett, *J. Phys. Chem.*, 1964, **68**, 3318.
[5] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 1958, **28**, 719.
[6] E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, 1962, **84**, 685.