Chemical Communications
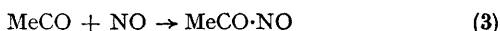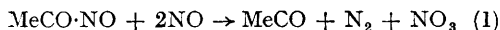
Intermediates in the Photochemical Reaction of Acetone with Nitric Oxide

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WHEN acetone is photolysed in presence of nitric oxide ($\ll$ 60 mm.) nitrogen dioxide is formed[1] according to the equation $d[NO_2]/dt = kI_a[NO]^2$ where I_a is the intensity of light absorbed. The formation of nitrogen dioxide is attributed to the reaction of MeCO·NO with nitric oxide producing the following chain:

$$MeCO·NO + 2NO \rightarrow MeCO + N_2 + NO_3 \quad (1)$$

$$NO_3 + NO \rightarrow 2\,NO_2 \quad\quad\quad\quad (3)$$

$$MeCO + NO \rightarrow MeCO·NO \quad\quad (3)$$

$$2\,MeCO·NO \rightarrow products \quad\quad\quad (4)$$

The MeCO·NO rapidly reaches a steady state during photolysis; two minutes after photolysis the only monomeric nitroso-compound present is nitrosomethane detected by its reaction (to form nitrogen dioxide) with a larger pressure (*ca.* 300 mm.) of nitric oxide. If, however, 300 mm. of nitric oxide is added immediately after photolysis, more nitrogen dioxide is produced than can be accounted for by the nitrosomethane. The Figure illustrates this effect. When allowance is made for the $d[NO_2]/dt$ ($=x$) produced from the nitrosomethane it is apparent that the active intermediate disappears in a first-order reaction, $t_{\frac{1}{2}} = 12$ sec. Within the limit $\pm$ 2 sec. the half-life is independent of nitric oxide pressure (0·1—10 mm.), of acetone pressure (5—80 mm.), of added nitrogen dioxide (0·3 mm.), and of temperature (20—60°). The yield of active intermediate is independent of nitric

oxide pressure down to at least 10^{-2} mm. The reaction leading to the production of nitrogen dioxide in the dark immediately after photolysis exhibits the same kinetics as does the photolytic reaction *i.e.*, $d[NO_2]/dt = k[Me_2CO]^{\frac{1}{2}}[NO]^2$, under conditions where I_a is proportional to acetone pressure.
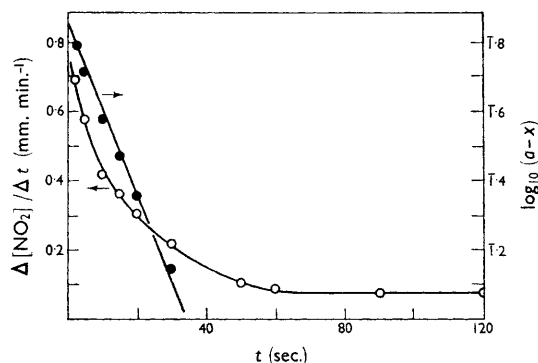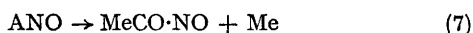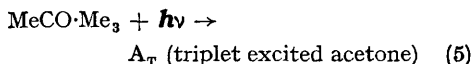

FIGURE   30 *mm. of acetone photolysed for* 1 *min. in presence of* 0·1 *mm. of nitric oxide*: 300 *mm. of nitric oxide added* t *sec. after irradiation.*

○ *Plot of* $\Delta[NO_2]/\Delta t$ (= a) *against* t.

● *Plot of* log_{10} (a—x) *against* t; x = $\Delta[NO_2]/\Delta t$, *measured after* 2 *min.*

The production of nitrogen dioxide in the photolysis of acetaldehyde–nitric oxide mixtures has also been attributed[1] to the intermediate

MeCO·NO. The half-life of the active species found to be present in this system is 7 sec. The facts that the disappearance of the intermediate is first order and not second order as is required kinetically for MeCO·NO and that $t_{\frac{1}{2}}$ for the active species formed in the acetaldehyde system differs from that for the acetone system suggest that the intermediate is not MeCO·NO itself but a precursor of it. It is suggested that the intermediate is formed in the reaction of nitric oxide with triplet excited molecules. The simplest scheme accounting for the acetone results is:

$$MeCO·Me_3 + h\nu \rightarrow$$
$$A_T \text{ (triplet excited acetone)} \quad (5)$$

$$A_T + NO \rightarrow ANO \quad (6)$$

$$ANO \rightarrow MeCO·NO + Me \quad (7)$$

Steady-state treatment for reactions (1) to (7) leads to $d[NO_2]/dt = 2k_1[\Phi_5 I_a/k_4]^{\frac{1}{2}}[NO]^2$ in accord with experiment. Since the rate of production of nitrogen dioxide is proportional to the square root of the concentration of ANO the half-life of reaction (7) is half the experimental $t_{\frac{1}{2}}$ i.e., 6 sec. for ANO. Corresponding values for the species formed in the acetaldehyde, diethyl ketone, and di-n-propyl ketone systems are, respectively, 3·5, 4, and 4 sec. With the di-isopropyl ketone system no dark reaction with nitric oxide was observed, apart from that of nitrosoisopropane.

The reaction of nitric oxide with triplet excited acetone is known to be rapid; the rate constant can be estimated[2,3] to be $> 10^{10}$ l.mole^{-1}sec.$^{-1}$ It has often been suggested[3–5] that the deactivation of triplet excited acetone by molecules such as nitric oxide, oxygen, and iodine may involve chemical reaction. Recently direct evidence for a rapid chemical reaction between triplet excited acetone and hydrogen bromide has been obtained.[6]

For the experiments reported above a broad wave-band (2400—3200 Å) from a stabilised xenon lamp was used. Both singlet and triplet acetone will be produced[5] and MeCO·NO may be formed from acetyl radicals arising from the dissociation of the excited singlet as well as from ANO. At the low pressures of nitric oxide used, reaction of the excited singlet with nitric oxide cannot compete with the other processes which the excited singlet can undergo.

Measurement of $\Phi(MeNO)$ at 3130 Å where $\Phi(A_T)$ in the absence of nitric oxide approaches unity provides further evidence for the reaction between A_T and nitric oxide. Quantum yields much greater than can be accounted for[5] by thermal dissociation of A_T are obtained, e.g., preliminary measurements of $\Phi(MeNO)$ formed in the irradiation of 25 mm. of acetone in presence of 5 mm. of nitric oxide at 20° indicate a value of about one, whereas the yield of methyl radicals in the absence of nitric oxide[5] is about 0·06 at this temperature.

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