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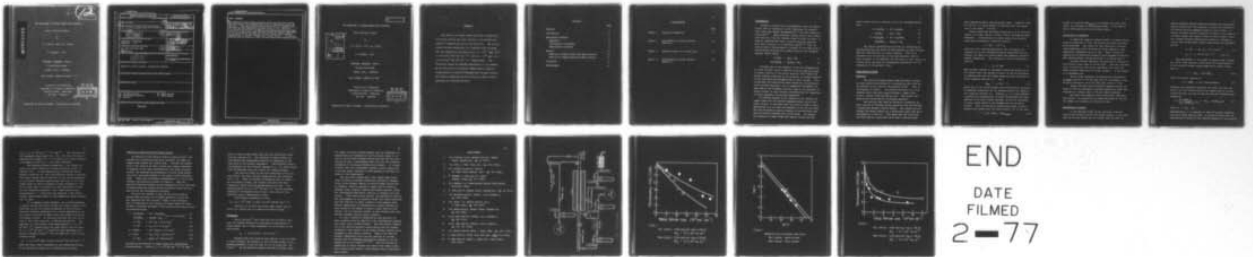
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THE REACTIONS OF OXYGEN ATOMS WITH NITRATES

Final Technical Report

By

L.F. Salter and B.A. Thrush

8 November 1976

EUROPEAN RESEARCH OFFICE

United States Army

London, N.W.1., England.

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ABSTRACT

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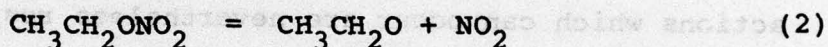
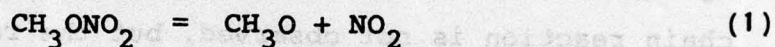
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Introduction

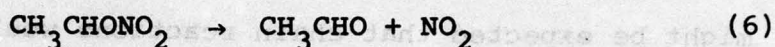
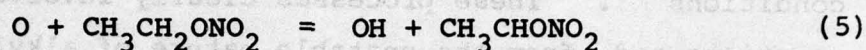
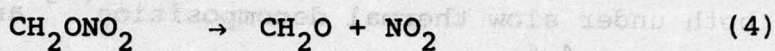
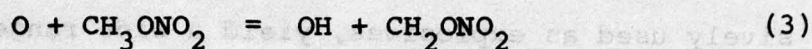
Aliphatic nitrates and nitrocompounds, which are extensively used as explosives, yield a wide range of products, both under slow thermal decomposition¹⁻³ and under explosive conditions⁴⁻⁶. These processes clearly involve free radical reactions and, from the unstable nature of alkyl nitrates, it might be expected that chain reactions would be important. With alkyl nitrates, it is generally agreed^{1,2,6} that the initial step in the pyrolysis is rupture of the O-NO₂ bond to yield nitrogen dioxide and a highly reactive, but thermally unstable alkoxy radical



Although many of the products of the slow decomposition of alkyl nitrates would be expected to arise from the attack of alkoxy radicals on the parent molecule, Levy² found that ethoxy radicals generated by the pyrolysis of diethyl peroxide do not accelerate the decomposition of ethyl nitrate. This illustrates the difficulties which attend the interpretation of the nitrate pyrolyses, and no unambiguous assignment has been made of the secondary reaction steps in the pyrolysis of methyl nitrate or ethyl nitrate notwithstanding the importance of these compounds as prototype explosives.

In previous studies of the kinetics of the reaction of oxygen atoms with the related compounds methyl nitrite and ethyl nitrite, it was shown that the initial attack involved abstraction of a hydrogen atom adjacent to the nitrite group. This was followed by exoergic rupture of the molecular fragment to yield an aldehyde plus nitric oxide. By analogy, the reaction of oxygen atoms with methyl nitrate and with

ethyl nitrate would be expected to have the analogous mechanism :



The results presented here confirm this mechanism and thereby show that the attack of free radicals on alkyl nitrates does not lead directly to a chain reaction. This is in agreement with the kinetics of the slow pyrolysis, where a chain reaction is not observed, but the range of free radical reactions which can occur are nevertheless responsible for the complexity of the products found.

Experimental Methods

Apparatus

The reaction between oxygen atoms and methyl nitrate or ethyl nitrate was studied in a low pressure fast flow system similar to that used for the previous study⁷. This is illustrated in figure 1. The reactor consisted of a 25 mm diameter pyrex tube which passed through a copper-lined electric furnace which was 900 mm long. The furnace temperature was controlled by a Eurotherm regulator.

The reaction time could be varied by introducing the alkyl nitrate at different points along the flow tube through a grease-less movable injector system. The reagent was fed through fine Tygon tubing into a narrow-bore glass tube which terminated in a fine jet. This glass tube was slid along the flow tube by a frictional drive from a rotating shaft

which passed through a cone and socket joint. Reaction times of 0.02 to 1.0 s could readily be obtained with total pressures in the range 1 - 10 Torr.

Atomic oxygen was generated by passing ca 1% of molecular oxygen in an argon carrier through a 200 W, 2450 MHz microwave discharge. Concentrations of atomic oxygen were measured using the stoichiometric titration reaction



using an R.C.A. 1P28 photomultiplier cell to measure the intensity of the air afterglow produced downstream from the furnace exit where the flowing gases had completely cooled to ambient temperature. The intensity of the air afterglow is given by

$$I = I_0 [\text{O}] [\text{NO}] \quad (\text{i})$$

When nitrogen dioxide is introduced through the mixing jet at the furnace exit, the maximum intensity of the air afterglow is observed when half the oxygen atoms have been converted to nitric oxide by reaction (7). Thus

$$I_{\text{MAX}} = I_0 [\text{O}]_0^2 / 4 \quad (\text{ii})$$

where $[\text{O}]_0$ is the initial oxygen atom concentration, providing an absolute calibration for the photomultiplier cell based on the titration reaction (7). Knowing I_0 , it is then possible to measure the concentration of oxygen atoms before and after addition of an alkyl nitrate upstream, as well as the amount of nitric oxide formed in the decomposition of the alkyl nitrate. This is achieved by adding known flows of nitric oxide at the furnace exit and using relation (i) in the form

$$I = I_0 [\text{O}] ([\text{NO}]_f + [\text{NO}]_{\text{added}}) \quad (\text{iii})$$

A plot of I against $[\text{NO}]_{\text{added}}$ is a straight line with slope $I_0[\text{O}]$, and intercept on the abscissa equal to the flow of nitric oxide emerging from the furnace $[\text{NO}]_f$.

Purification of Reagents

A commercial sample of methyl nitrate of nominal purity 99.8% was distilled at 193K, the initial and final fractions being discarded. The liquid was then subjected to several freeze-pump-thaw cycles followed by direct pumping at room temperature immediately prior to use. Ethyl nitrate was supplied by the Explosives Research and Development Establishment (Waltham Abbey) and was purified in a similar manner.

Nitrogen dioxide (Matheson) was purified by successive distillation using traps at 77K and 193K. This was continued until the solid was pure white, indicating that water and other nitrogen oxides were no longer present. It was stored in a blackened bulb.

Nitric oxide (Matheson) was purified by distillation in vacuo from 90K to 77K and from 113K to 77K through a trap containing molecular sieve and soda lime cooled to 113K.

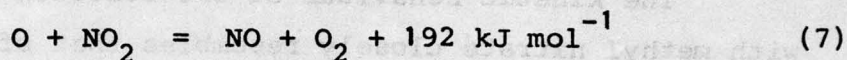
Oxygen and argon were purified by passage through two traps at 193K and atmospheric pressure packed with glass wool followed by a similar trap at 77K and reduced pressure.

Gas flows were measured using conventional capillary flow meters: the calibration of these was based on, but did not assume, the validity of Poiseuille's Law.

Experimental Procedure

In the previous study⁷ of the reactions of methyl nitrite and of ethyl nitrite with atomic oxygen, it was shown that the initial attack was the slowest step and that the

species produced reacted relatively rapidly with more atomic oxygen to yield the final products, in which the nitrogen of the initial molecule appeared solely as nitric oxide. A similar situation would be expected to obtain in the reaction of atomic oxygen with methyl nitrate or ethyl nitrate, since any nitrogen dioxide produced would rapidly be reduced to nitric oxide by the excess atomic oxygen which was invariably present

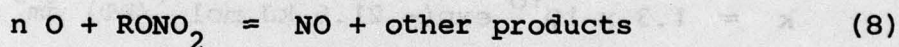


$$k_7 = 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{ref. 8})$$

Thus measurement of the number of oxygen atoms consumed per nitric oxide molecule formed gives the stoichiometry (n) of the reaction between oxygen atoms and an alkyl nitrate. That is

$$n = ([O]_0 - [O]) / [NO]_f \quad (\text{iii})$$

where the overall reaction is



Providing the subsequent reactions are rapid, the rate constant k for the initial attack of an oxygen atom on an alkyl nitrate molecule can then be derived from the integrated rate expression

$$\ln \frac{[O] [RONO_2]_0}{[O]_0 ([RONO_2]_0 - x)} = ([O]_0 - n[RONO_2]_0)kt \quad (\text{iv})$$

$$\text{where } nx = [O]_0 - [O]$$

Experimentally, it is simplest to vary the nitrate concentration for a fixed reaction time. It should be noted that any contribution by atoms or free radicals produced in the reaction

to the initial attack on the alkyl nitrate molecule will increase the nitric oxide yield, reduce the measured stoichiometry n and hence increase the value of k derived from relation (iv).

Results

Reaction of Oxygen Atoms with Methyl Nitrate

The kinetic behaviour of the reaction of oxygen atoms with methyl nitrate closely resembles that of the reaction of oxygen atoms with methyl nitrite⁷. The measured reaction stoichiometry is close to 6 and decreases with increasing substrate flow due to reactions between product radicals and methyl nitrate (figure 2).

Since both the mechanisms discussed below give stoichiometries of $n = 6$, the limiting values of the rate coefficient at low methyl nitrate concentrations were calculated for $n = 6$. These are given in Arrhenius form in figure 3, where the best straight line corresponds to the rate expression

$$k = 1.3 \times 10^{10} \exp(-21.6 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

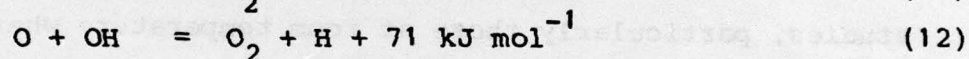
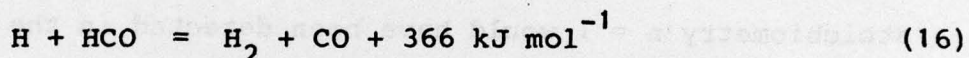
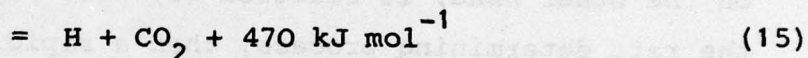
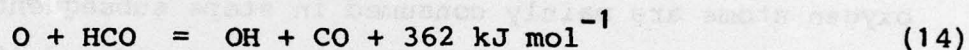
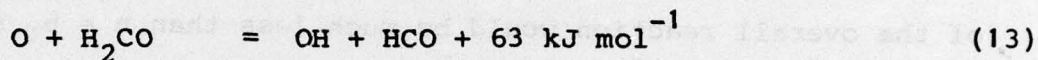
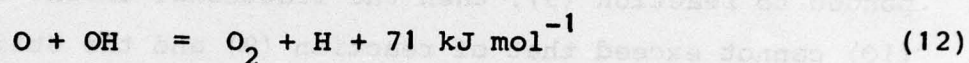
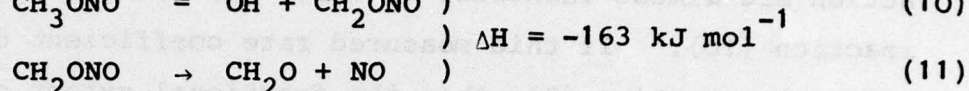
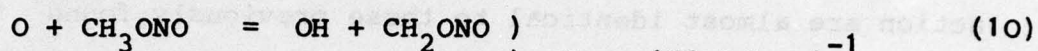
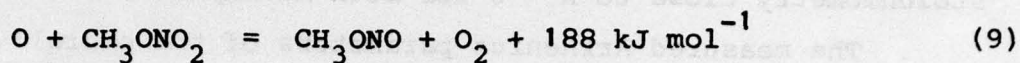
For the reaction of oxygen atoms with methyl nitrite, a closely similar value was obtained for the corresponding Arrhenius expression⁷

$$k = 1.4 \times 10^{10} \exp(-21.8 \pm 2.0 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

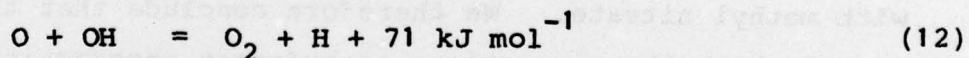
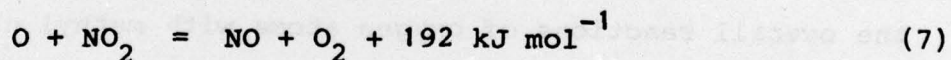
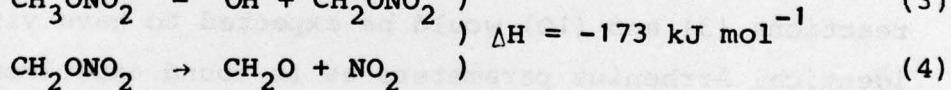
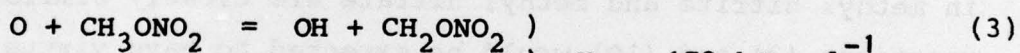
There are two mechanisms for the reaction between oxygen atoms and methyl nitrate which would give the required stoichiometry of $n = 6$ and are basically consistent with the previous results on the reaction of oxygen atoms with methyl nitrite and other compounds^{7,9,10}.

If the initial step involves abstraction of an oxygen

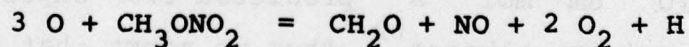
atom from the methyl nitrate, the reaction of oxygen atoms with methyl nitrite which has an overall stoichiometry of $n = 5$ would follow :



The other mechanism starts, like the methyl nitrite reaction, with hydrogen abstraction



In both mechanisms, the reaction of oxygen atoms with methyl nitrate and the subsequent steps give the stoichiometry



This is followed by the reaction of oxygen atoms and formaldehyde which goes virtually to completion since its initial step (13) has a rate coefficient more than ten times that found here for the reaction of oxygen atoms with methyl nitrate

($k_{13} = 9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300K^{10}). This reaction and the subsequent rapid steps (12), (14), (15) and (16) give an observed stoichiometry of $n = 2.8$, making the overall reaction stoichiometry close to $n = 6$ for both mechanisms.

The measured Arrhenius parameters of the overall reaction are almost identical to those previously found⁷ for reaction (10). If this measured rate coefficient corresponded to reaction (9), then the fractional extent of reaction (10) cannot exceed that of reaction (9) and the stoichiometry of the overall reaction would be much less than $n = 6$, since oxygen atoms are mainly consumed in steps subsequent to (10). On the other hand, if reaction (9) were rapid and (10) were the rate determining process, then a rapid reaction with stoichiometry $n = 1$ would have been detected in the kinetic studies, particularly those at room temperature where reaction (10) is slow.

If, as appears highly probable, the C-H bond strengths in methyl nitrite and methyl nitrate are closely similar, then reactions (3) and (10) would be expected to have virtually identical Arrhenius parameters as is found experimentally for the overall reactions of oxygen atoms with methyl nitrite and with methyl nitrate. We therefore conclude that the initial step in both these reactions is hydrogen abstraction. For reaction (3), the A-factor found experimentally ($1.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) agrees within the error limits with the value of $1.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ predicted from experiments on a series of primary alkanes¹², thus we adopt that value for the A-factor giving

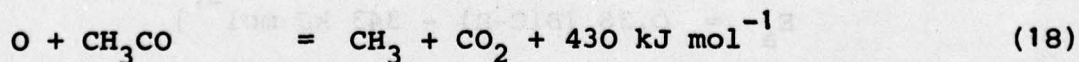
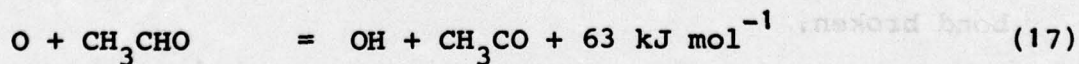
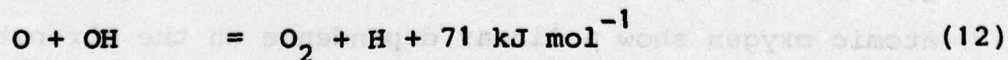
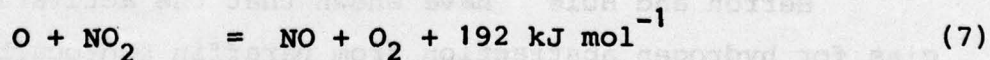
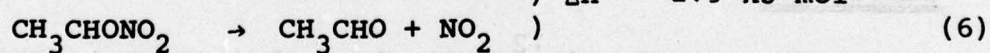
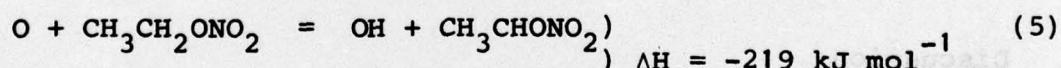
$$k_3 = 1.5 \times 10^{10} \exp(-22.0 \pm 1.0 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

where the error limits correspond to two standard deviations of the activation energy with a predetermined A-factor.

Reaction of Oxygen Atoms with Ethyl Nitrate

As observed in the previous study of ethyl nitrite⁷, the presence of an additional CH₂ group increases the number of oxygen atoms removed per initial step. Although the greater rate of the reaction of ethyl nitrate with oxygen atoms made it possible to use lower concentrations than those of methyl nitrate, the measured stoichiometries of nitric oxide production still rose quite sharply at low ethyl nitrate concentrations. These gave intercepts corresponding to $n \approx 10$ at zero reactant concentration as shown in figure 4. Thus the observed difference between the stoichiometries of the reactions of oxygen atoms with methyl nitrate and ethyl nitrate are the same as with the corresponding nitrites⁷.

This, and the increase in rate of the initial step on passing from the methyl to the ethyl derivative, which was also observed with the nitrites⁷, leads to the conclusion that the mechanism of the reaction of oxygen atoms with ethyl nitrate is strictly analogous to the reaction with ethyl nitrite, the mechanism being



followed by the reaction of oxygen atoms with formaldehyde discussed above. Since $k_{17} = 3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300K¹¹,

which is thirty times faster than the rate coefficient found here for reaction (5). The reactions of oxygen atoms with acetaldehyde and formaldehyde would go to completion on the time scale of the present experiments. The predicted overall stoichiometry for this reaction sequence is $n = 10$, which agrees with the measured value well within its limited accuracy.

The limiting values of the rate coefficient of the initial step at low ethyl nitrate concentrations were evaluated for $n = 10$. These are plotted in Arrhenius form in figure 3. As with methyl nitrate, the accuracy with which the pre-exponential factor could be determined was not high. The predicted value of $2.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for two secondary hydrogens¹² was adopted since it lay in the centre of the possible range of experimental values.

The Arrhenius expression is then

$$k_5 = 2.6 \times 10^{10} \exp(-21.6 \pm 2.6 \text{ kJ mol}^{-1} / RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Reaction (5) is more than three times faster than reaction (3), partly due to a smaller activation energy.

Discussion

Herron and Huie¹² have shown that the activation energies for hydrogen abstraction from paraffin hydrocarbons by atomic oxygen show a linear dependence on the strength of the bond broken:

$$E_a = 0.36 [D(\text{C-H}) - 343 \text{ kJ mol}^{-1}]$$

Assuming that this relation also applies to the C-H bonds in alkyl nitrates, the energies of the C-H bonds broken in the primary processes (3) and (5) must lie in the range 400 - 405 kJ mol^{-1} . As was found with methyl and ethyl nitrites, these

are normal C-H bond energies showing that the exothermic re-organisation and fragmentation of the radical formed in (3) and (5) occurs after hydrogen abstraction and that the possibility of such a rearrangement does not alter the Arrhenius parameters of the process forming this radical. It is most unlikely that this intermediate radical could be stabilised in the gas phase, although it could perhaps be isolated in a matrix at low temperatures.

The conclusion reached here, that oxygen atoms attack alkyl nitrates by hydrogen abstraction followed by decomposition of the primary radical to yield nitrogen dioxide and an aldehyde, would be expected to apply also to attack by hydrogen atoms, hydroxyl radicals and alkoxy radicals, where the corresponding abstraction reaction is somewhat more exothermic. With these latter species, the abstraction reaction and rearrangement of the products yields only stable molecules. Thus the stability of alkyl nitrates at and somewhat above ambient temperatures is determined by a balance between the easy fission of the $RO-NO_2$ to yield a highly reactive free radical, and the efficient removal of such radicals when they abstract hydrogen from the parent molecule.

On such a simplistic mechanism, the slow pyrolysis of alkyl nitrates would be expected to the corresponding aldehyde and alcohol plus nitrogen dioxide. The much greater complexity of the observed products arises partly from the thermal instability, particularly of the larger alkoxy radicals which decompose to give smaller radicals. Many of the observed products undoubtedly arise from the reaction of nitrogen dioxide with the aldehydes and alcohols produced in the decomposition of the nitrate^{1,6,13,14}. Thus the thermal decomposition of alkyl nitrates can yield a wide range of products without being itself a chain process with a significant chain length.

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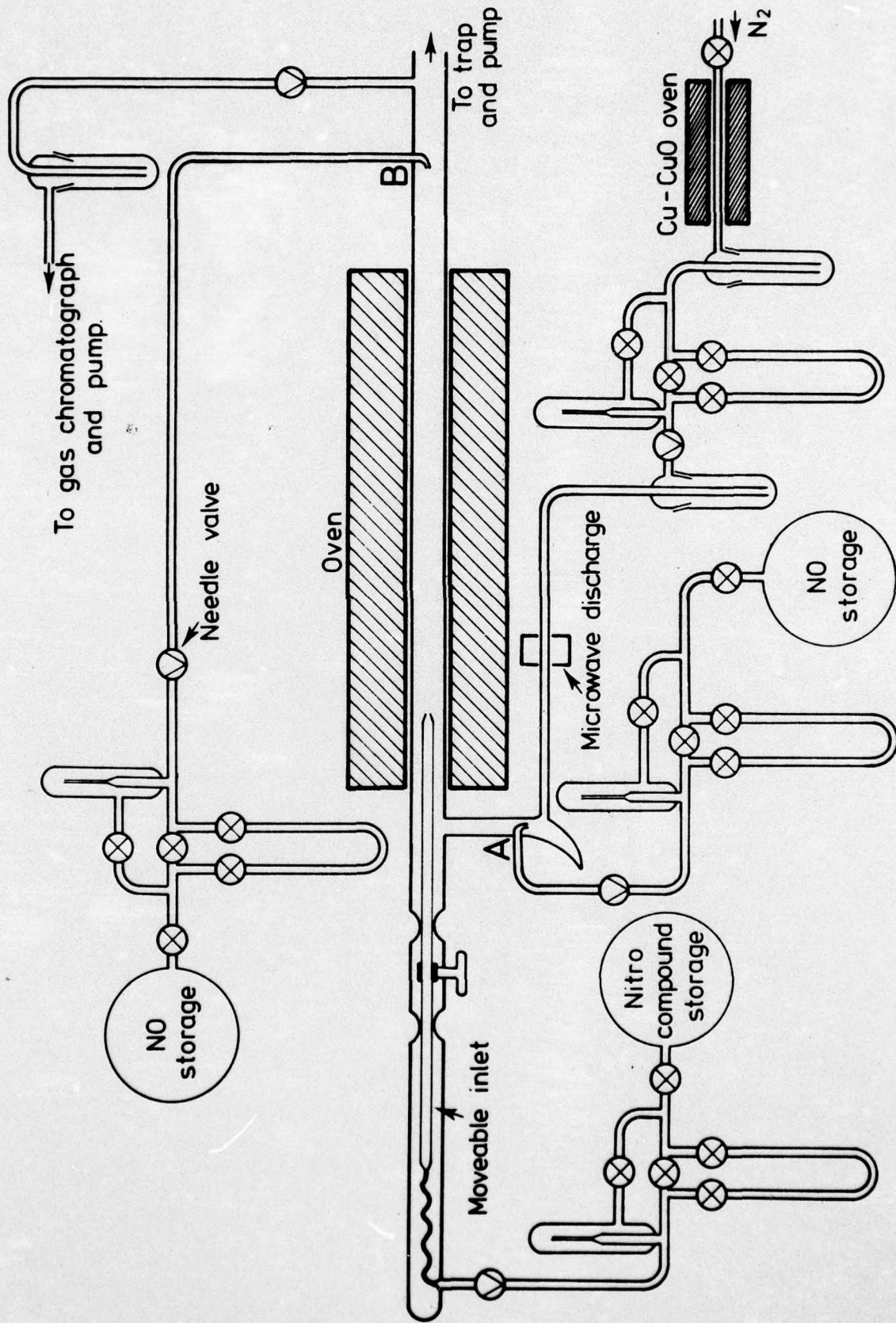


FIGURE 1 DIAGRAM OF FLOW APPARATUS.

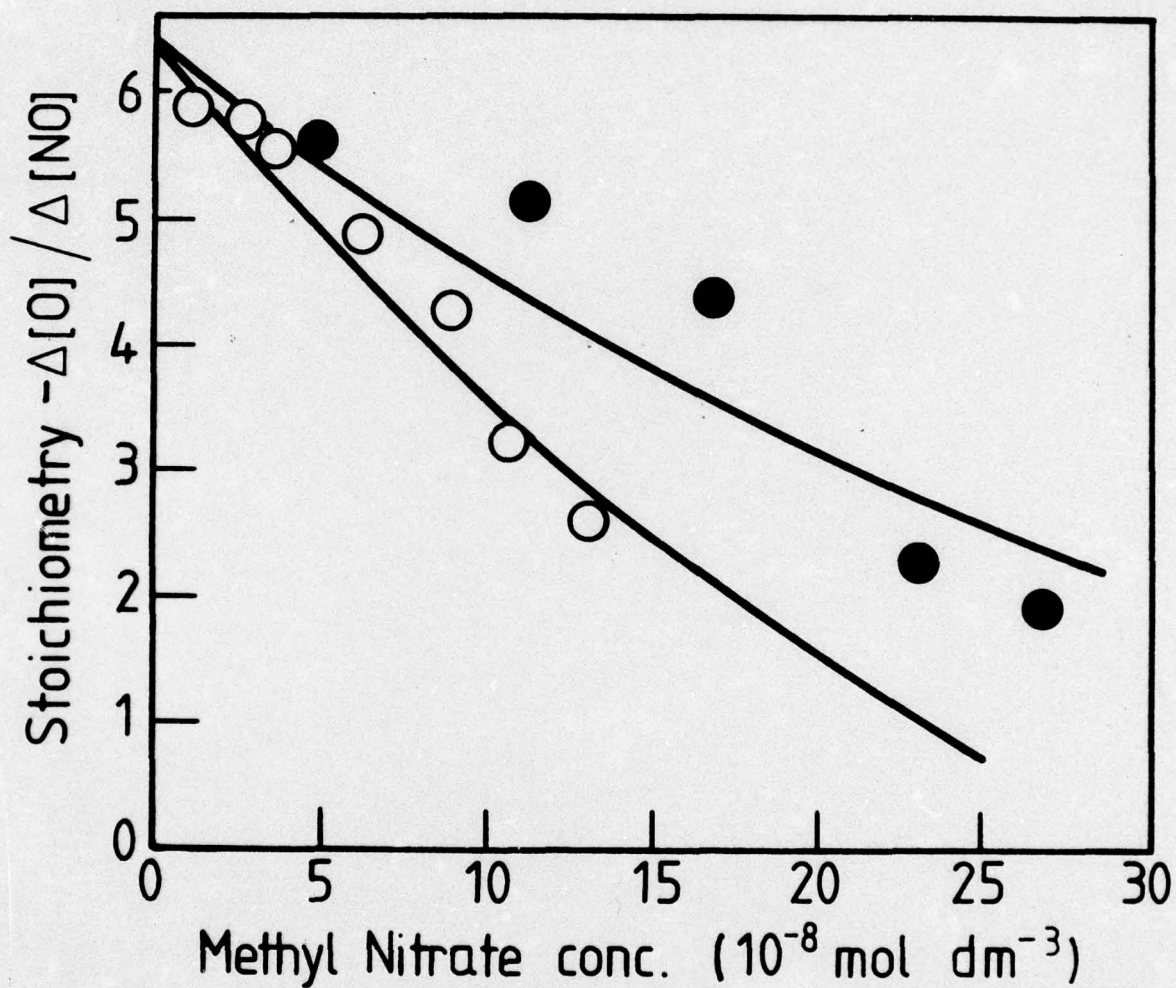


FIGURE 2

FULL CIRCLES: 0.40s REACTION TIME AT 294.4K;
 $[\text{O}]_0 = 9.5 \times 10^{-8} \text{ MOL DM}^{-3}$

OPEN CIRCLES: 0.24s REACTION TIME AT 383.2K;
 $[\text{O}]_0 = 4.5 \times 10^{-8} \text{ MOL DM}^{-3}$

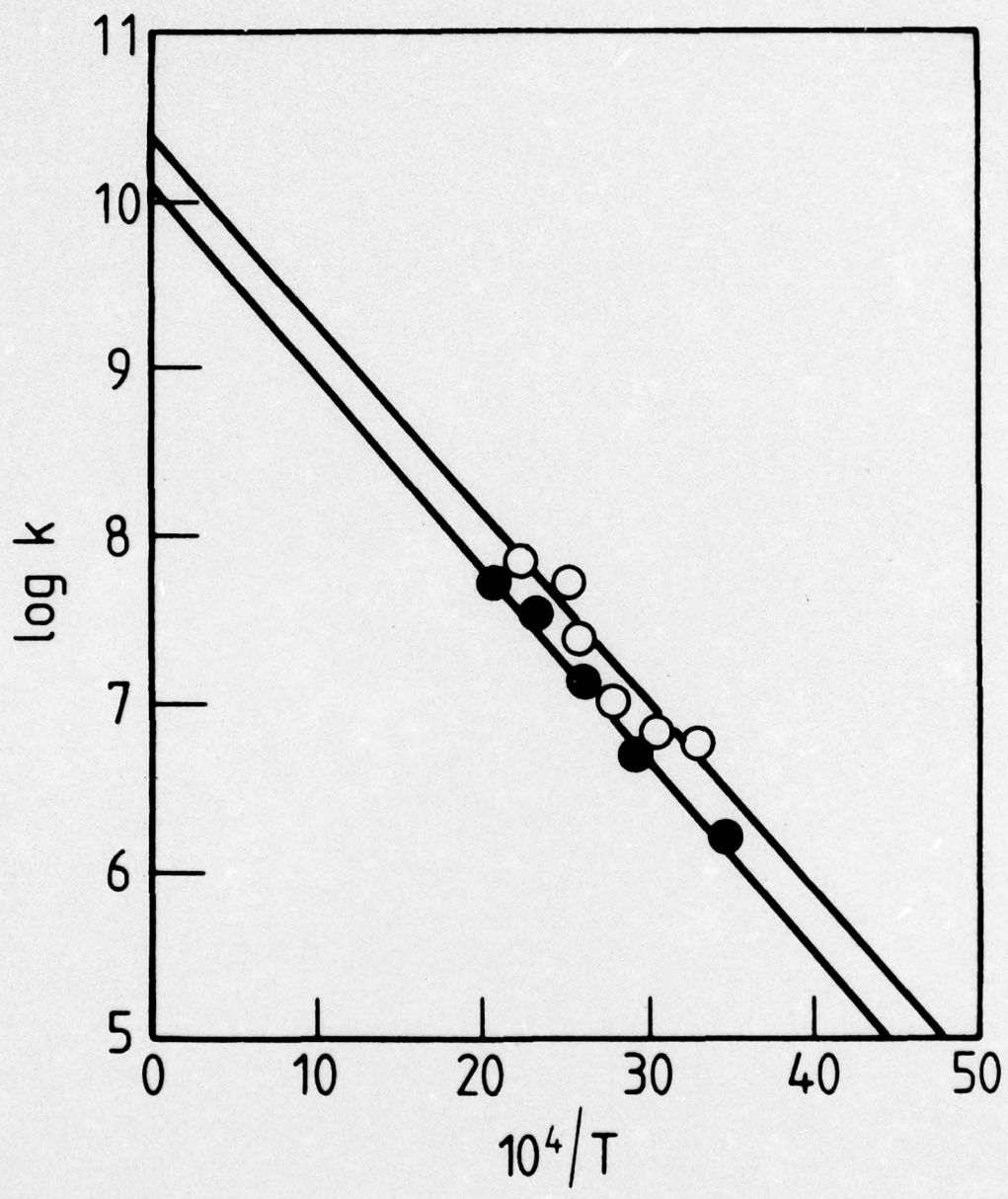


FIGURE 3

ARRHENIUS PLOTS FOR OXYGEN ATOM ATTACK

FULL CIRCLES: METHYL NITRATE

OPEN CIRCLES: ETHYL NITRATE

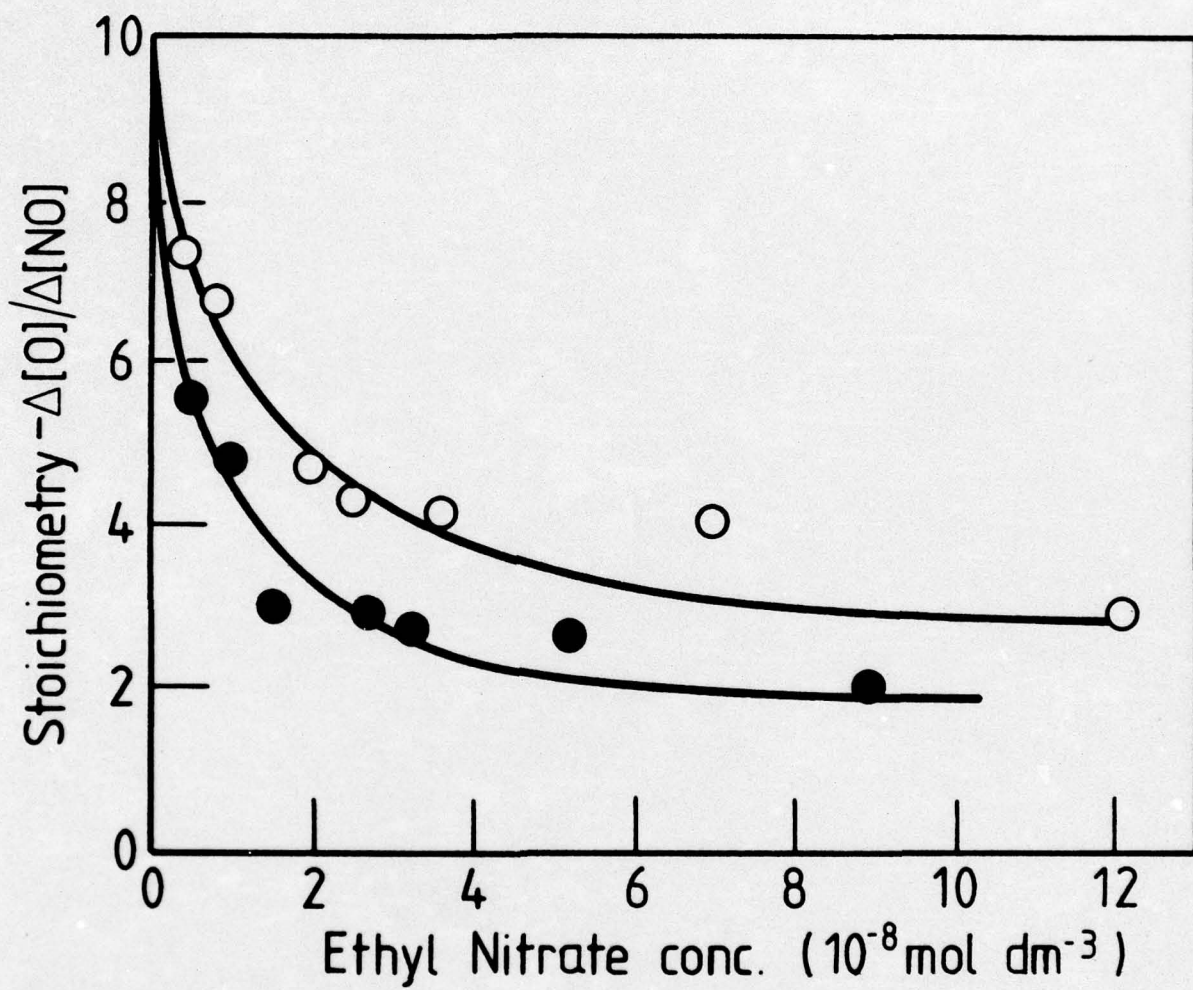


FIGURE 4

FULL CIRCLES: 0.30s REACTION TIME AT 300.2K;
 $[O]_0 = 2.7 \times 10^{-7} \text{ MOL DM}^{-3}$

OPEN CIRCLES: 0.25s REACTION TIME AT 333.2K;
 $[O]_0 = 2.5 \times 10^{-7} \text{ MOL DM}^{-3}$