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Citation: The Journal of Chemical Physics **37**, 1233 (1962); doi: 10.1063/1.1733270 View online: http://dx.doi.org/10.1063/1.1733270 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/37/6?ver=pdfcov Published by the AIP Publishing

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CONCLUSIONS

place as the polymerization proceeds.

It has been shown that through measurements of proton spin-lattice relaxation time it is possible to obtain an insight into the molecular processes that take place during polymerization.

We have seen that the motional processes which govern nuclear magnetic relaxation are independent of the flow viscosity. Moreover the temperature dependence of nuclear relaxation allows us to consider such motions to be thermally activated. The activation energies increase slowly as the polymerization proceeds and we have therefore a slow decrease of the spinlattice relaxation time T_1 of the monomer molecules that are still present dispersed among the polymer chains.

The experimental results obtained for the activation energies have been explained by admitting that a distribution of correlation frequencies for molecular motion is present during the polymerization process and that its width increases as the polymerization proceeds. The existence of such a distribution has been admitted many times in the study of polymers and has been confirmed by dielectric-loss measurements.

We think that our results are of some interest particularly because the presence of a distribution of correlation frequencies is not immediately apparent from NMR measurements.

ACKNOWLEDGMENTS

The authors are indebted to Professor L. Giulotto for many helpful suggestions and for his interest in this work.

The authors also take pleasure in acknowledging many stimulating discussions with Dr. F. Borsa and Dr. P. Mascheretti.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 37, NUMBER 6 **SEPTEMBER 15, 1962**

Mass Spectrometric Studies of Atomic Reactions. III. Reactions of Hydrogen Atoms with Nitrogen Dioxide and with Ozone*

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The reaction of H atoms with excess NO_2 results in the production of one NO molecule for every NO_2 molecule consumed and the consumption of 1.5 ± 0.1 NO₂ molecules per H atom initially present. The secondary reactions are rapid and make the over-all reaction very suitable for H-atom titration. A mechanism is proposed to explain these results. The reaction of H atoms with excess O_a results in the consumption of 3.1 ± 0.2 O₃ molecules for each H atom initially present. Addition of H₂ and N₂O to the system showed that vibrationally excited OH formed in the initial reaction decomposes O₃. Other mechanisms for the additional O₃ consumption are discussed. The rate constant for the primary step was found to be $(4.8\pm0.5)\times$ 10^{-11} cm³ molecule⁻¹ sec⁻¹ for the NO₂ reaction and $(2.6\pm0.5)\times10^{-11}$ cm³ molecule⁻¹ sec⁻¹ for the O₃ reaction tion.

THE reaction of hydrogen atoms with ozone is now L generally conceded to be a major source of the Meinel OH bands in the night sky.

$$H+O_3 \rightarrow OH^{\ddagger}+O_2 \cdots . \tag{1}$$

Laboratory studies of this very rapid reaction have been mainly limited to spectral measurements of the emission, and only rough estimates of the rate are available. The present work is concerned with determining the rate constant for the primary reaction and the nature of the secondary reactions of the excited OH radical produced.

Hydroxyl radicals may also be obtained from the

reaction of H atoms with NO₂:

 $H+NO_2 \rightarrow NO+OH+30 \text{ kcal} \cdots$ (2)

This reaction is analogous to reaction (1) but should be kinetically simpler because of the greater stability of NO₂ relative to O₃ which might lead to a reduction in the number of secondary reactions. Moreover, Del Greco and Kaufman¹ have found that the OH produced from this reaction possesses little, if any, vibrational excitation. For these reasons, this reaction was also fully investigated.

EXPERIMENTAL

The details of the apparatus have been described previously.² It consisted of a microwave discharge to

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^{*} This work was supported in part by the U.S.Air Force Cambridge Research Laboratories and in part by the Defence Research Board of Canada.

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¹ F. Del Greco and F. Kaufman, Discussions Faraday Soc. (to be published). ² L. F. Phillips and H. I. Schiff, J. Chem. Phys. 36, 1509

^{(1962).}



FIG. 1. "Titration" curves for the reaction of H atoms with NO₂ and with O₃; reaction time, 25 msec. \bigcirc —partial pressure of NO₂; O—partial pressure of O₃; ---- initial H-atom concentration.

produce the H atoms, a fast flow system including a movable inlet for introduction of the O_3 or NO_2 , and a mass spectrometer for measuring the concentration of reactants and products as a function of time after initiation of the reaction. The flow of NO_2 was controlled by a needle valve, while the flow of the equimolar $Ar-O_3$ mixture was controlled by passing it through a capillary containing a close-fitting rod, the length of which could be varied by a magnetically manipulated iron slug enclosed in glass. The movable inlet consisted of a 6-mm glass sphere having six equally spaced holes, 0.04 mm in diameter, circumferentially distributed at right angles to the gas flow.

Because of the rapidity of these reactions, H_2 was diluted with a several-hundredfold excess of He or Ar. The gases were passed over heated copper and through traps immersed in liquid air or dry ice. Because the hydrogen could readily be dissociated to 50% by the discharge, the concentration of H atoms could be determined with an accuracy of about 5% from the decrease in the ion current (peak height) at mass 2 when the discharge was activated. Comparison of the decrease in peak height at mass 2 with the increase at mass 1 indicated that the mass spectrometric sensitivity of H atoms is 0.24 times the sensitivity for H_2 at mass 2. Determinations of very low H-atom concentrations were affected by "titration" with excess NO₂, since it was found that 1.5 NO2 molecules are consumed for each H atom reacted. Carbon and rhenium filaments were used in the mass spectrometer.

RESULTS

The reaction of H atoms with O_3 is accompanied by a peach-colored flame due to vibrational overtones of OH. The H-NO₂ reaction is accompanied by a rather bright emission similar to the familiar NO-O "airglow." This suggests that O atoms play an important role in this system and must be considered in any postulated mechanism.

Figure 1 shows typical curves of the amount of O_3 and NO_2 destroyed for the *same* initial H-atom concentration as a function of the initial O_3 or NO_2 concentration. These measurements were made with a reaction time of 25 msec, and it is apparent that the reactions which consume NO_2 are faster than those which consume O_3 . The "plateau" values correspond to 1.5 ± 0.1 NO₂ molecules, and 3.1 ± 0.2 O₃ molecules consumed per H atom initially present.

Composition-time curves are shown for the $H-O_3$ reaction in Fig. 2 and for the $H-NO_2$ reaction in Fig. 3. Water and oxygen are seen to be major products of both reactions. The rapid rise of the H_2O curve should not be taken as evidence that it is formed in the initial reaction, since recombination of OH in the leak or in the ion source may occur to a large extent. When the O_3 inlet was in the form of a single 0.1-mm jet and only 1 mm from the leak, the ratio of peak heights at masses 18 and 17 decreased by about 10%, but the amount of H_2O formed was still so large that no accurate estimate of the OH concentration could be made.

The amount of NO produced in the H-NO₂ reaction will be seen to equal the amount of NO₂ consumed. This agrees with the results of Clyne and Thrush.³ However, these authors report only one NO₂ molecule consumed per H atom originally present, in disagreement with the present findings. At NO₂ partial pressures of 10^{-2} mm or greater, a white deposit was



FIG. 2. The concentration-time dependence in the reaction of H atoms with O₃. (a) excess O₃: \bigcirc -H×10³; \bigcirc -O₃×10³; \bigcirc -O₃×10⁴; \bigcirc -O₂×10⁸. (b) excess H atoms: \bigcirc -H×10³; \bigcirc -O₃×10³; \bigcirc -H₂O×10³; \bigcirc -O₂×10³.

³ M. A. A. Clyne and B. A. Thrush, Trans. Faraday Soc. 57, 2176 (1961).

noticed on the walls of the reaction vessel. This deposit could be removed by pumping for a short time. A similar deposit was also noticed by Del Greco and Kaufman¹ and was identified as ammonium nitrate. In the present work, the deposit was detected on the rims of the NO₂-inlet holes, which suggests that it was produced by a heterogeneous reaction. Homogeneous reactions would have to be impossibly fast to lead to so complex a product. The nitrogen and oxygen mass balances obtained indicate that this deposit is only a minor product of the reaction.

DISCUSSION

Reaction of H Atoms with NO₂

The following sequence of reactions is consistent with the observations:

 $H+NO_2 \rightarrow NO+OH;$

 $OH+OH\rightarrow H_2O+O;$

$$k = 2.5 \times 10^{-12}$$
 (reference 1). (3)

(2)

 $O+OH\rightarrow O_2+H;$

 $k=1-2\times 10^{-11}$ (reference 1). (4)

 $O+NO_2 \rightarrow NO+O_2;$

$$k = 2.5 \times 10^{-12}$$
 (reference 2). (5)

These reactions explain the observed products (except for the small amount of solid NH_4NO_3) and are consistent with the over-all stoichiometry. Oxygen



FIG. 3. The concentration-time dependence for the reaction of H atoms with NO₂. (a) excess NO₂. \bigcirc -NO×10³; \bigcirc -NO₂×10⁴; \bigcirc -H₂O×10⁴; \bigcirc -O₂×10⁴; \bigcirc -H×10³. (b) excess H atoms: \bigcirc -NO×10³; \bigcirc -NO₂×10³; \bigcirc -H₂O×10³; \bigcirc -O₂×10³; \bigcirc -H×10³.



FIG. 4. The change in O_3 decomposition by H atoms upon addition of H_2 and N_2O . $\bigcirc -H_2$; $\bigcirc -N_2O$.

atoms are consumed mainly by reaction (4) for low NO_2 concentrations and by reaction (5) for high NO_2 concentrations. However, in either case the over-all stoichiometry remains the same, viz.,

$$2 \text{ H}+3 \text{ NO}_2 \rightarrow 3 \text{ NO}+\text{O}_2+\text{H}_2\text{O}.$$

One NO molecule will be formed for each NO₂ consumed, and 1.5 NO_2 molecules will be consumed for each H atom reacted, in agreement with observation. The rapidity of the reactions explains the "titration" behavior and suggests the reaction as a very suitable method for determining H-atom concentrations.

If excess NO₂ is present, O₂ will continue to increase after all the H atoms are consumed as a result of reactions (4) and (5). If H atoms are present in excess, O₂ will be produced only by reaction (4). This explains why O₂ production is faster in Fig. 3(a) than in Fig. 3(b), although approximately the same number of OH radicals has been produced in both cases. These observations are consistent with the rate constants reported in reference 1.

The alternative paths for OH radical recombination are:

$$OH+OH\rightarrow H_2O_2\cdots$$
 (6)

$$\rightarrow$$
H₂+O₂··· (7)

$$\rightarrow HO_2 + H \cdots$$
 (8)

Reaction (8) need not be considered since it is highly endothermic. Reaction (6) probably requires a third body. Back and Ung^4 have found that it is an important process at relatively high pressures (30 mm).

⁴ R. Back and A. Y. M. Ung (private communication).

Partial pressures (mm Hg)									
t msec	Argon	Helium	$10^4(H_2)$ total	104[O ₃] ₀	10⁴[H]₀	10 ⁴ y ^a	$k_1 \times 10^{11}$ cm ³ molecule ⁻¹ sec ⁻¹		
1.55	0.407	•••	28.4	4.5	12.0	2.95	2.2		
2.3	0.407	•••	28.4	3.95	12.0	3.05	1.9		
3.1	0.407	•••	28.4	3.65	12.0	3.3	2.5		
3.9	0.407	•••	28.4	2.8	12.0	2.7	2.4		
1.55	0.407	•••	17.9	5.75	8.85	3.2	2.3		
2.3	0.407	•••	17.9	5.1	8.85	3.5	2.2		
3.1	0.407	•••	17.9	4.2	8.85	3.3	2.3		
3.9	0.407	•••	17.9	3.95	8.85	3.55	2.4		
1.1	•••	0.470	7.65	8.8	4.35	2.7	3.6		
2.2	•••	0.470	7.65	8.25	4.35	3.3	3.2		
3.35	•••	0.470	7.65	8.8	4.35	3.8	3.1		
4.45	•••	0.470	7.65	8.8	4.35	4.0	2.8		
5.55	•••	0.470	7.65	8.7	4.35	4.1	3.2		
1.25	•••	0.405	17.4	8.7	3.2	1.9	2.9		
1.9	•••	0.405	17.4	8.95	3.2	2.45	2.9		
2.5	•••	0.405	17.4	8.7	3.2	2.7	3.1		
3.1	•••	0.405	17.4	8.95	3.2	2.95	3.2		
3.75	•••	0.405	17.4	8.5	3.2	3.0	3.2		
1.25	•••	0.405	14.8	14.2	3.05	1.9	1.9		
2.5	•••	0.405	14.8	14.6	3.05	2.7	2.2		
3.75	•••	0.405	14.8	14.3	3.05	2.95	2.3		
1.25	•••	0.405	14.8	20.4	2.9	2.45	2.3		
2.5	•••	0.405	14.8	19.8	2.9	2.7	1.9		
3.75	•••	0.405	14.8	19.5	2.9	2.85	2.2		
Mean $k_1 = (2.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^3$									

TABLE I. $H+O_3 \rightarrow OH+O_2$.

^a $y = (O_3)_0 - (O_3)_t$.

Reaction (7) is considered unlikely, since it is a fourcenter reaction. Reaction (3) is the only reaction which produces O atoms, the presence of which is clearly indicated by the NO-O chemiluminescence. It is also the only recombination step capable of explaining the over-all stoichiometry.⁵ If the maximum uncertainty in the observed stoichiometry is ascribed to reactions (6) and (7), they could at most account for 30% of the OH recombination.

The following reactions will also be too slow to be important in this system:

$$OH + NO_2 \rightarrow HO_2 + NO \cdots,$$
 (9)

$$OH + H \rightarrow H_2 + O \cdots, \tag{10}$$

$$OH+H_2 \rightarrow H_2 O+H\cdots, \qquad (11)$$

$$O+H_2 \rightarrow OH+H\cdots, \qquad (12)$$

$$O_2 + H \rightarrow OH + O \cdots$$
 (13)

Ternary or wall recombinations will also be too slow to compete with reactions (2)-(5), although a small increase in peak height at mass 31 suggests the production of a trace amount of HNO.

Reaction of H Atoms with O₃

The primary step in this reaction is undoubtedly

$$H+O_3 \rightarrow OH+O_2 \cdots$$
 (1)

By analogy with the NO₂-H reaction, the following secondary reactions would be expected:

$$OH+OH \rightarrow H_2O+O\cdots, \tag{3}$$

$$O + O H \rightarrow O_2 + H \cdots, \tag{4}$$

$$O+O_3 \rightarrow 2 O_2 \cdots$$
, $k=2.5 \times 10^{-14}$ (reference 2). (14)

However, in this case, $k_4 \gg k_{14}$, which explains the lack of sharpness of the titration curve. In curve 2(a), the O₃ concentration continues to decrease and the O₂

 $^{^{6}}$ It is very unlikely that any radical formed by subsequent reactions of H₂O₂ could result in a net removal of 1.5 NO₂ molecules and still produce one NO per NO₂ consumed.

Partial pressures (mm Hg)											
t msec	Argon	Helium	104[H2] total	104[NO2]0	10⁴[H]₀	10⁴ <i>y</i> ≞	$k_2 \times 10^{11}$ cm ³ molecule ⁻¹ sec ⁻¹				
1.1	0.462		19.2	8.65	14.2	7.3	5.2				
1.8	0.462		19.2	8.65	14.2	7.6	4.2				
2.5	0.462	•••	19.2	8.45	14.2	8.05	4.7				
3.2	0.462		19.2	8.45	14.2	8.2	4.5				
1.4	0.462	•••	19.2	14.0	14.0	10.0	4.2				
2.1	0.462	•••	19.2	14.0	14.0	11.1	4.0				
2.75	0.462	•••	19.2	14.0	14.0	11.7	4.2				
3.45	0.462	•••	19.2	14.0	14.0	12.3	4.5				
4,15	0.462	•••	19.2	14.0	14.0	12.6	4.7				
4.8	0.462	•••	19.2	14.0	14.0	12.7	4.3				
1.4	0.462	•••	19.2	25.3	14.3	13.8	5.0				
2.1	0.462	•••	19.2	24.7	14.3	14.1	4.7				
1.12	•••	0.398	25.6	7.3	12.8	6.0	5.3				
1.7	•••	0.398	25.6	7.3	12.8	6.5	5.0				
2.25	•••	0.398	25.6	7.3	12.8	6.7	4.3				
2.8	•••	0.398	25.6	7.3	12.8	6.95	4.5				
1.12		0.398	25.6	13.0	13.0	9.25	5.2				
1.7	•••	0.398	25.6	13.0	13.0	10.3	5.3				
2.25		0.398	25.6	13.0	13.0	10.9	5.5				
2.8		0.398	25.6	13.0	13.0	11.2	5.3				
3.4	•••	0.398	25.6	13.0	13.0	11.35	4.8				
3.9	•••	0.398	25.6	13.0	13.0	11.5	4.7				
1.12	•••	0.398	18.4	15.0	10.0	7.4	4.7				
1.7		0.398	18.4	14.8	10.0	8.2	5.0				
2.25	•••	0.398	18.4	14.8	10.0	8.65	5.5				
2.8	•••	0.398	18.4	14.0	10.0	8.45	4.2				
Mean $k_2 = (4.8 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.											

TABLE II. $H+NO_2 \rightarrow OH+NO$.

^a $y = (NO_2)_t - (NO_2)$.

concentration to increase after the H atoms have all been consumed because of reaction (14), there being insufficient OH radicals to consume all the O atoms.

On the basis of this mechanism the over-all stoichiometry would be

$$2 \text{ H}+3 \text{ O}_3 \rightarrow 4 \text{ O}_2 + \text{H}_2\text{O}$$

while the experiment showed that 3.1 ± 0.2 O₃ molecules were consumed per H atom reacted when excess ozone was present. There are three possible explanations for this result.

a. Regeneration of H atoms

By the reaction

$$OH+H_2 \rightarrow H+H_2O\cdots$$
,

Avramenko and Lorentso⁶ have reported a value of approximately 1×10^{-16} cm³ molecule⁻¹ sec⁻¹ for k_{15} at 300°K. Del Greco and Kaufman¹ have suggested that this rate constant may be as large as 10^{-14} at 300°K. The rate of this reaction may be even higher in the present system if the OH molecules are vibrationally excited. Under these conditions, this reaction might be capable of competing successfully with (3) and (4).

b. Chain Decomposition of O_3

Consisting of the reaction

 $OH+O_3 \rightarrow HO_2+O_2\cdots$, (16)

⁶L. I. Avramenko and R. N. Lorentso, Zhur. Fiz. Khim. 32, 1193 (1958).

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(15)

along with any of the chain-carrying reactions

$$HO_2 + O_3 \rightarrow OH + 2 O_2 \cdots, \qquad (17)$$

$$HO_2 + H_2 \rightarrow OH + H_2O \cdots,$$
 (18)

$$HO_2 + H \rightarrow OH + OH \cdots$$
 (19)

Reaction (18) is probably not important, since it involves considerable rearrangement and should therefore be slower than reaction (12). The chain termination steps would be reaction (3) and

$$HO_2 + OH \rightarrow H_2O + O_2 \cdots,$$
 (20)

$$HO_2 + H \rightarrow H_2 + O_2 \cdots, \qquad (21)$$

$$\rightarrow$$
H₂O+O···, (22)

$$O + HO_2 \rightarrow OH + O_2 \cdots$$
 (23)

This mechanism is supported by the observation of a small, but definite increase in the mass 33 peak when the discharge is excited, indicating the presence of HO_2 radicals in the system. This peak was found to decrease with time in a way analagous to the decrease in the 17/18 peak ratio, which suggests that HO_2 radicals are formed in reactions involving OH. No increase at mass 34 corresponding to H_2O_2 was ever detected.

c. Reaction involving excited OH[‡]

Reaction (1) is exothermic to the extent of 77 kcal, and it is known that all or part of this energy may appear as vibrational excitation of the OH radicals. These excited radicals could decompose O_3 :

$$OH^{\ddagger}+O_{3}\rightarrow OH+O_{2}+O\cdots$$
 (24)

This reaction is analogous to the decomposition of O_3 by N_2^{\dagger} formed in the reaction of N atoms with NO,⁷ which is exothermic to the extent of 75 kcal.

Reactions (1), (24), (3), or (4), and (14) are capable of accounting for the consumption of 3.5 O_3 molecules per H atoms compared with the maximum value of 3.3 found experimentally. The average value of 3.1 would correspond to 80% of the OH molecules, formed initially, being capable of decomposing O_3 , in rather close agreement with the figure found for the N_2^{\dagger} molecules formed in the NO-N reaction.

In order to distinguish between these three possibilities, H_2 and N_2O were added to the gas stream $\overline{{}^7 \text{ L. F. Phillips}}$ and H. I. Schiff, J. Chem. Phys. **36**, 3283 (1962). through an auxiliary inlet located between the discharge and the O_3 inlet.

If possibility (a) were correct, addition of H_2 would increase the amount of O_3 decomposition while addition of N_2O would have no effect. In the case of (b) no effect should be noted when either gas is added. In the case of (c) addition of both gases should deactivate OH[‡] and the amount of O_3 decomposition should be decreased.

The results of these experiments, shown in Fig. 4, clearly indicate a decrease in ΔO_3 with increasing amount of added gas. Nitrous oxide is approximately 2.5 times as effective as H_2 . The absence of any reaction between N₂O and any free radicals in the system was indicated by the absence of any change in the peak heights at masses 44 and 28 when the discharge was excited. These results can be taken as clear evidence for the occurrence of reaction (24). However, the ratio of Δ [O₃]/[H]₀ did not reduce to the value of 1.5 as required by the simple mechanism (1), (3), (4), and (14). It is therefore possible that reaction (15) or, more likely, reaction (16) occurs to some extent. Inclusion of reaction (16) alone raises the ratio to 2.0, which is not an unreasonable limit to Fig. 4 at high concentration of added N₂O. There is, however, no reason to suspect the occurrence of chain reactions in this system.

Rates of Initial Reactions

Because the initial reactions are extremely rapid in comparison with the secondary reactions, it was possible to determine the rate constants for reactions (1) and (2) separately. To do this, however, it was necessary to use very low reagent concentrations. For partial pressures of reagents below 0.5 μ , the stoichiometry for both reactions was found to be 1:1, and the ordinary rate expressions for second-order reactions could be used to obtain the rate constants.

The results of these determinations are shown in Tables I and II. Mean rate constants and standard deviations are given at the foot of each table. The experimental error is estimated to be about 25% for both rate constants. The value of k_2 is in reasonable agreement with the value of 5×10^{-11} cm³ molecule⁻¹ sec⁻¹ found by Rosser and Wise⁸ at 500°C by a completely independent method.

⁸ W. A. Rosser and H. Wise, J. Phys. Chem. 65, 532 (1961).