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Reactions of Nitrogen Dioxide with Other Gases

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Nitrogen dioxide is dissociated by ultraviolet radiation according to reaction (I)

$NO_2 + h\nu \longrightarrow 2NO + O$[1] (I)

The primary dissociation process is believed to be[2]

$$NO_2 + h\nu(3900 - 2600\ \text{Å.}) \longrightarrow NO + (^3P)O \qquad \text{(IIa)}$$

and

$$NO_2 + h\nu(\lambda < 2460\ \text{Å.}) \longrightarrow NO + (^1D)O \qquad \text{(IIb)}$$

Thus by irradiating NO_2, one may obtain either normal (^3P) oxygen atoms or excited (^1D) oxygen atoms, depending on the spectral region used for the irradiation. It should be possible, therefore, to study the behavior of normal and excited oxygen atoms by noting the effects produced when gas mixtures containing NO_2 are irradiated with ultraviolet light. One difficulty with such experiments is that the oxygen atoms produced by irradiation react with the NO_2 present at a very fast rate according to reaction (III)[3,4]

$$NO_2 + O \longrightarrow NO + O_2 \qquad \text{(III)}$$

The study of the reaction of oxygen atoms produced by the photolysis of nitrogen dioxide is limited to those gases which are not dissociated by the radiation used and which do not react with nitrogen dioxide in the dark. Several gases were studied. A low (1 to 10 mm.) partial pressure of nitrogen dioxide was used to minimize reaction (III).

Experimental

Method of Measurement.—The nitrogen dioxide and the other gas, each at a known pressure, were introduced into the reaction cell. Reaction was indicated by the net change in the partial pressure of NO_2, as determined photometrically. The products of reaction were determined from the changes in total pressure and from the ultraviolet absorption spectra of the reacted mixtures.

The reaction vessel consisted of a quartz cylindrical cell (22.1 cm. long, 3 cm. diameter) having plane parallel windows at each end. The cell was provided with tubulations, which led to a quartz spiral manometer, to a freeze-out trap and to the filling systems. After the proper amount of nitrogen dioxide and the other reactant had been introduced into the freeze-out trap (cooled to −195°), the reaction vessel was sealed off from the filling system. The reacting gases were in contact with glass and quartz surfaces only. Pressure measurements, as determined by the balance of the spiral manometer and made with a Société Génévoise cathetometer, were reproducible to 0.02 mm. The photometer system (described elsewhere presently) permitted reproducible readings to at least 0.05 mm. for the partial pressure of NO_2. A no. 315 Hilger spectrograph was used to photograph the absorption spectra of some of the reaction mixtures. For this purpose, the products were transferred to another quartz cell with light path of 12.1 cm. Eastman I-O plates were used to record the spectra.

Ultraviolet Radiation.—A quartz mercury arc lamp (600 watts input) with a glass filter served as one source of ultraviolet radiation. The glass filter used in conjunction with this lamp was found to transmit only radiation of wave length longer than 310 mμ.

A cadmium spark, operated from a transformer supplying 7000 volts and a 0.04 mf. condenser (primary input 60 amperes at 220 volts) in conjunction with a chlorine–bromine filter (l = 2 cm., p = 1 atm), served as the source of radiation for shorter wave lengths (220–270 mμ). The ultraviolet radiation was brought to a focus at the center of the reaction cell by two large condensing lenses.

Preparation of Gases.—The preparation and purification of the nitrogen dioxide have been described.[5] *Hydrogen chloride* was prepared from hydrochloric acid and sulfuric acid. *Carbon monoxide* was prepared from 85% formic acid and concentrated sulfuric acid. The gas was purified by passage through an alkaline solution of pyrogallol and was dried by passage through phosphorus pentoxide. *Methyl alcohol* and *carbon disulfide* were obtained from c. p. products. *Methane* and *ethylene* were obtained from commercial cylinders of the compressed gases. Each of the substances except carbon monoxide was subjected to partial distillation before being introduced into the reaction vessel.

1. Reactions of Methyl Alcohol and of Hydrogen Chloride with Nitrogen Dioxide.—(a) Reaction between nitrogen dioxide and methyl alcohol occurred in the dark at room temperature as the gases sublimed from the condensed state. In an experiment where the initial partial pressures of nitrogen dioxide and methyl alcohol were 2.4 mm. and 19.6 mm., respectively, 85% of the nitrogen dioxide was found to have reacted by the time the gases had completely sublimed. Twenty-five minutes later, 98% of the original nitrogen dioxide had reacted. The products of

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(1) R. G. W. Norrish, *J. Chem. Soc.*, 761 (1927); R. G. Dickinson and W. P. Baxter, THIS JOURNAL, **50**, 774 (1928); H. H. Holmes and F. Daniels, *ibid.*, **56**, 630 (1934).

(2) V. Henri, *Nature*, **125**, 202 (1930).

(3) H. J. Schumacher, THIS JOURNAL, **52**, 2584 (1930).

(4) F. C. Henriques, Jr., A. B. F. Duncan and W. A. Noyes, Jr., *J. Chem. Phys.*, **6**, 518 (1938).

(5) L. Harris, G. W. King, W. S. Benedict and R. W. B. Pearse, *J. Chem. Phys.*, **8**, 765 (1940).

TABLE I

Reaction vessel at 25°. Pressures in millimeters of mercury reduced to 0°. The freeze-out trap was cooled to −195°, warmed to room temperature and the system allowed to remain at room temperature for 22 to 26 hours before the final pressure readings were made. The final p_{CS_2} was obtained from final p_{total}, final p_{NO_2}, and the mole changes involved; p_{NO_2} at termination of irradiation was obtained by extrapolation of NO_2 transmission measurements taken three to four minutes after irradiation was terminated; p_{CS_2} at termination of irradiation was assumed to be the same as p_{CS_2} final.

		Init. p				P at end of irrad.		Final p			
Run	Irrad., min.	Total	NO_2	N_2O_4	CS_2	NO_2	N_2O_4	Total	NO_2	N_2O_4	CS_2
1a	10	5.00	1.53	0.07	3.42	0.30	..	5.33	0.66	0.02	3.15
2	10	12.05	7.20	.44	4.43	3.55	0.20	12.65	5.91	0.30	4.00
1b	37	5.00	1.53	.07	3.42	0.05	..	5.41	0.07	..	2.76
3	40	6.35	4.74	.22	1.39	0.78	0.02	7.11	3.02	0.16	0.99

this reaction were not identified. However, nitric oxide was not present among the products.

(b) The dark reaction between nitrogen dioxide and hydrogen chloride was also rapid at room temperature. In an experiment where the initial partial pressures of nitrogen dioxide and hydrogen chloride were 3.5 and 8.3 mm., respectively, 50% of the nitrogen dioxide had reacted before completion of sublimation.

Ten minutes later, 85% of the original nitrogen dioxide had disappeared. Condensation of the resulting mixture to liquid nitrogen temperature gave yellow crystals characteristic of nitrosyl chloride. This observation and measurements of the change in total pressure indicate the reaction

$$NO_2 + 2HCl \longrightarrow NOCl + H_2O + {}^1/_2Cl_2 \quad (IV)$$

Nitric oxide was not found among the products.

2. Reactions of Carbon Monoxide and of Methane with Nitrogen Dioxide.—(a) Nitrogen dioxide–carbon monoxide mixtures: A number of experiments were made with such mixtures, in which the partial pressure of carbon monoxide varied from 5.0 to 6.0 mm. and the partial pressure of nitrogen dioxide varied from 1.5 to 3.0 mm. No dark reaction was observed at room temperature, nor at temperatures as high as 250°. No photochemical reaction involving carbon monoxide occurred (with either source of radiation), even when the cell temperature was raised to 250°. At 300° the dark reaction became measurable; at 350° the rate became quite appreciable, 55% of the nitrogen dioxide having reacted in three hours. Nitric oxide was found to be one of the reaction products; carbon dioxide was presumably the other product. Irradiation of nitrogen dioxide–carbon monoxide mixtures at 330° with the shorter wave length ultraviolet resulted in reaction of 15% of the nitrogen dioxide in one and one-half hours, approximately the same rate as for the dark reaction at this temperature. Similar results were obtained by Crist and Roehling,[6] who found that the rate of oxidation of carbon monoxide by mixtures of nitrogen dioxide and oxygen was not influenced by irradiation with light of wave length 3650 Å. The slow rate of oxidation of carbon monoxide by oxygen atoms was demonstrated by Harteck and Kopsch,[7] who mixed oxygen atoms, obtained from a discharge tube, with carbon monoxide. Our measurements indicate that the rate of reaction of nitrogen dioxide with either (^{3}P) or (^{1}D) oxygen atoms is much faster than the rate of combination of oxygen atoms with carbon monoxide.

(b) Methane–nitrogen dioxide mixtures: The range of partial pressures in this study was the same as that in the carbon monoxide experiments.

The methane mixtures did not react in the dark, nor was any appreciable thermal reaction observed below 300°. Ultraviolet radiation of either wave length region did not initiate reaction nor did the radiation have any measurable effect upon the thermal reaction above 300°. One of the products of this reaction is nitric oxide.

Since the rate of reaction of methane with oxygen atoms is comparatively slow,[7] we conclude that the oxygen atoms formed by the photolysis of nitrogen dioxide react with the residual nitrogen dioxide at a much faster rate than they react with methane.

3. Reactions of Carbon Disulfide and of Ethylene with Nitrogen Dioxide at Room Temperature.—(a) Carbon disulfide–nitrogen dioxide mixtures: No dark reaction was observed for the nitrogen dioxide–carbon disulfide mixtures, nor was any reaction observed when the mixtures were illuminated with radiation of wave length longer than 410 mμ. Reaction occurred when the mixtures were subjected to ultraviolet radiation ($\lambda > 310$ mμ). The measurements on three runs are given in Table I.

The products of reaction identified were nitric oxide, sulfur dioxide and carbonyl sulfide. When

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[6] R. H. Crist and O. C. Roehling, THIS JOURNAL, **57**, 2200 (1935).

[7] P. Harteck and U. Kopsch, *Naturwissenschaften*, **17**, 727 (1929); *Z. physik. Chem.*, **B12**, 327 (1931).

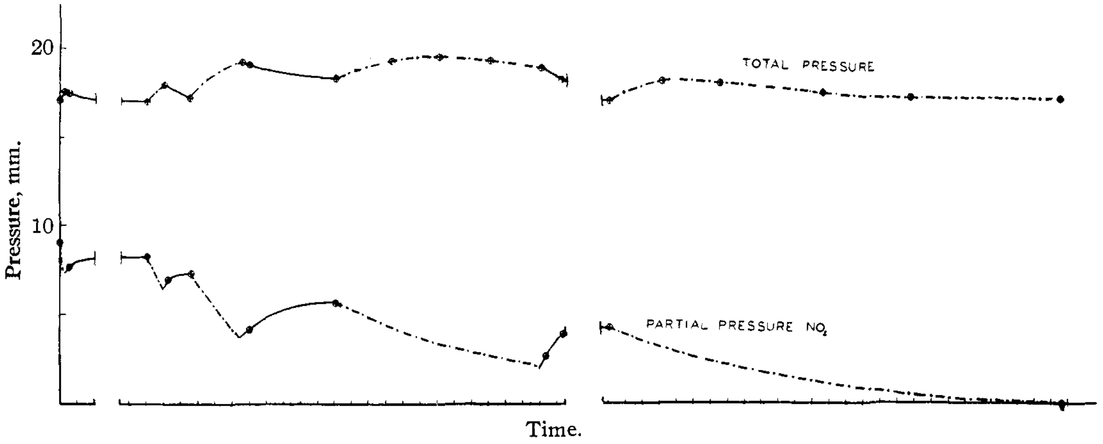

Fig. 1.—Full lines represent dark reaction intervals; dotted lines represent irradiation intervals. The time scale is divided into five-minute intervals, except for two gaps; the time interval for the first gap is five hours; for the second gap, eleven hours.

mixtures rich in carbon disulfide (runs 1 and 2) were irradiated, a deposit of sulfur was formed on the walls of the reaction cell. Carbon monoxide, carbon dioxide and sulfur trioxide probably were also produced.

A series of spectrograms was recorded after each stage of irradiation. The temperature of the freeze-out trap was varied from −195 to 25° for each series. The presence of nitric oxide and sulfur dioxide was deduced from the banded structure of the spectrograms; the presence of carbonyl sulfide from the continuous absorption below 255 mμ.[8] The absorption due to each of these components increased in intensity as irradiation was continued. (The presence of nitric oxide was also demonstrated by the fact that the original concentration of nitrogen dioxide was regenerated when air was admitted to the system.) A small residual pressure in the system when the freeze-out trap was immersed in liquid nitrogen indicated the presence of carbon monoxide.

Since carbon disulfide is not decomposed by the radiation used,[9] photochemical reaction is initiated by the oxygen atoms produced from the photolysis of the nitrogen dioxide. Oxygen atoms may react with carbon disulfide according to reactions Va and Vb.

$$CS_2 + O \longrightarrow CS + SO \qquad (Va)$$

$$CS_2 + O \longrightarrow COS + S \qquad (Vb)$$

Reaction V is rapid; carbon disulfide competes with nitrogen dioxide for the photolyzed oxygen atoms. The relative rates of reactions (III) (rate = k_{III} [O] [NO_2]) and (V) (rate = k_V[O] [CS_2]) are calculated from the data given in Table I. Assuming the steady state, d[O]/dt = 0, and neglecting the effect of secondary reactions of nitrogen dioxide with the radicals formed

$$\frac{d[NO_2]}{d[CS_2]} = \frac{2k_{III}[NO_2] + k_V[CS_2]}{k_V[CS_2]} \qquad (VI)$$

Solving, $k_{III}/k_V = 3$. When account is taken of the nitrogen dioxide used in secondary reactions, $k_{III}/k_V \cong 2$. Henriques, Duncan and Noyes,[4] using the data of Spealman and Rodebush,[10] calculate the activation energy of (III) to be 4300 cal.

Using this value for the activation energy of the reaction of oxygen atoms with nitrogen dioxide, and making assumptions analogous to those made by Noyes and his co-workers,[4] we obtained an activation energy of 5000 cal. for the reaction of oxygen atoms with carbon disulfide.

(b) Ethylene–nitrogen dioxide mixtures: These gases did not react in the dark nor when irradiated with light of wave length longer than 410 mμ. Irradiation of gas mixtures with ultraviolet light ($\lambda > 310$ mμ) caused reaction to occur. The changes in total pressure and in the partial pressure of nitrogen dioxide, upon irradiation of a mixture of 9.10 mm. of nitrogen dioxide and 7.19 mm. of ethylene are shown in Fig. 1.

The *decrease* in partial pressure of NO_2 is twice as large as the total pressure *increase*, during the first twenty minutes of irradiation, indicating that no appreciable reaction of ethylene had occurred during that period. Upon additional

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(8) G. S. Forbes and J. E. Cline, THIS JOURNAL, **61**, 151 (1939).

(9) V. Henri, "Structure of Molecules," P. Debye, Blackie, Ltd., London, 1932, p. 129.

(10) M. L. Spealman and W. H. Rodebush, THIS JOURNAL, **57**, 1474 (1935).

irradiation, however, the total pressure reached a maximum value, while the partial pressure of NO_2 continued to decrease; from this we conclude that the ethylene had reacted at an appreciable rate after an induction period.

Nitric oxide was one of the final products, as shown by the absorption bands near 2260 Å. That ethylene oxide and acetaldehyde were among the final products was indicated by the pressure changes developed upon warming the freeze-out trap gradually from −195° to room temperature (after termination of irradiation and reaction). Additional oxidation products, besides the isomers of C_2H_4O, must have been formed since, although the original partial pressure of nitrogen dioxide was greater than that of ethylene, reaction proceeded to the exhaustion of the nitrogen dioxide.

Irradiation of ethylene–nitrogen dioxide mixtures with the shorter wave lengths of ultraviolet (270–220 mμ) also produced reaction. Preliminary experiments indicate a difference in behavior for this radiation than for the longer wave lengths of ultraviolet. Inasmuch as ethylene does not absorb the shorter wave length ultraviolet used, it should be ideal for the study outlined.

Conclusions

The two gases (carbon disulfide and ethylene) that were found to react with nitrogen dioxide when the gas mixtures were irradiated with ultraviolet light are known to react rapidly with oxygen atoms, while the two gases (carbon monoxide and methane) that did not react with nitrogen dioxide when the gas mixtures were irradiated, are known to react very slowly with oxygen atoms. Thus, Harteck and Kopsch[7] found that both carbon disulfide and ethylene reacted rapidly with the oxygen atoms obtained from a discharge tube, while methane and carbon monoxide reacted very slowly with oxygen atoms produced in this way. Our results show that oxygen atoms produced by the photolysis of nitrogen dioxide react with carbon disulfide and with ethylene at a rate comparable to the fast reaction of oxygen atoms and nitrogen dioxide.

Summary

Both methyl alcohol and hydrogen chloride react rapidly with nitrogen dioxide in the dark.

Neither carbon monoxide nor methane reacts with nitrogen dioxide in the dark or under the influence of ultraviolet radiation until the temperature of the gases is greater than 250°.

Neither carbon disulfide nor ethylene reacts with nitrogen dioxide in the dark at room temperature. Under the influence of ultraviolet radiation ($\lambda > 310$ mμ), however, each reacts with nitrogen dioxide at room temperature. The oxygen atoms produced in the photolysis of the nitrogen dioxide react rapidly with carbon disulfide and ethylene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

The Determination of α-Glycerophosphates in Aqueous Solutions by Means of Lead Tetraacetate

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Baer[1] finds that under certain conditions oxidations with lead tetraacetate can be performed in aqueous solutions. We have therefore utilized Carrara's[2] method employing this reagent to determine the percentage of calcium α-glycerophosphate in mixtures of the alpha and beta forms in aqueous solution.

Various factors have been found to affect the concordance and accuracy of these determinations. The presence of hydrochloric acid and of water is desirable to promote the solubility of the calcium or barium glycerophosphates, but too great a concentration of the acid or too much water causes loss of oxidizing power due apparently to hydrolysis of the tetraacetate. Again sufficient time must be given for the completion of the reaction, but treatment should not be continued too long, since under the conditions of analysis a spontaneous reduction of the tetraacetate takes place at the rate of 3% per day.

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(1) E. Baer, M. J. Grosheintz and H. O. L. Fischer, THIS JOURNAL, **61**, 2607 (1939).

(2) G. Carrara, *Giorn. Chim. ed. App.*, **14**, 236 (1932).