[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

A FURTHER STUDY OF THE REACTION BETWEEN NITROGEN DIOXIDE AND LIQUID MERCURY

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RECEIVED JUNE 6, 1928 PUBLISHED AUGUST 4, 1928

In an earlier article[1] a report was made of some experiments on the reaction, both thermal and photochemical, between nitrogen dioxide and liquid mercury. In that article it was reported that radiation of frequency greater than the threshold frequency of mercury caused the reaction to proceed more rapidly than in the dark. This effect was ascribed, at that time, to an activation of the mercury surface which was in some way associated with the photoelectric emission. In a somewhat later article[2] a revised explanation of the phenomenon was given in which the formation of negative ions due to the electron affinity of the nitrogen dioxide was suggested as the crucial factor in the acceleration of the reaction by short wave length radiation. Moore[3] has attempted to activate a mercury surface by electron bombardment. He offered a tentative explanation based on the formation of a monomolecular layer of mercuric oxide by the action of the filaments used. This film might hold mechanically any electrons emitted from the filament.

The experiments to be reported in this article were undertaken with the object of elucidating some of the factors involved in the reaction between mercury and nitrogen dioxide. The phenomena to be reported agree, in so far as they overlap, with results previously reported. It is, however, demonstrated that there are many variable factors, some of which are difficult, if not impossible, to control. A heterogeneous reaction of the type under consideration may be affected by many things such as the state of the surface, impurities in the gas and the possibility of the development of surface charges which lead to spurious effects. The present results may be deemed to be somewhat inconclusive, but they are reported at this time as it seems doubtful whether further experimentation along the lines indicated will lead to important results.

I. Preliminary Discussion

The reaction between liquid mercury and nitrogen dioxide presumably leads to the formation of mercuric oxide and nitrogen.[4] These final products are doubtless not formed quantitatively. The initial step in the process would seem to be, logically, the formation of a salt of the type of a

[1] Moore and Noyes, THIS JOURNAL, **46**, 1367 (1924).

[2] Noyes, *Trans. Faraday Soc.*, **21**, 569 (1926).

[3] Moore, THIS JOURNAL, **47**, 2932 (1925).

[4] Watts' "Dictionary of Chemistry," Longmans, Green and Co., London, **1894**, Vol. III, p. 566.

nitrite. Nitrogen dioxide has many of the characteristics of a free radical and possesses, as far as can be ascertained, an appreciable electron affinity.[5] One might expect the formation of a polar compound of the type of a mercurous (or mercuric) nitrite to be brought about by the transfer of an electron from the mercury to the nitrogen dioxide molecule. The reaction might be initiated, or accelerated, by the presence of negative ions in the nitrogen dioxide or by a positive charge on the mercury surface. In the experiments previously reported a large number (at least 10^8) molecules reacted per electron, assuming that the reaction with light is the sum of the normal dark plus the photochemical reaction. It is necessary, therefore, to postulate a chain mechanism to account for the results or to ascribe the action to the formation of nuclei on the surface.

The reaction between mercury and nitrogen dioxide is exothermic. If the activated state consists in the removal of the electron from the mercury, one should expect a relatively high energy of activation and consequently a high temperature coefficient for the reaction rate. The results to be reported indicate a low temperature coefficient. Since the reaction does not seem to be termolecular (or of higher order with respect to the pressure of nitrogen dioxide), the activated state for the dark reaction does not seem to be greatly different from the normal state. This means that the same proportion of the collisions between nitrogen dioxide molecules and the mercury surface will be effective regardless of temperature. The manner of the growth of the film indicates that nuclei on the surface act as centers of film formation. Since the number of molecules of gas hitting the surface will vary as the square root of the absolute temperature, the temperature coefficient of the reaction rate might be low if the reaction took place only around nuclei already present. However, the dependence of reaction rate on pressure of nitrogen dioxide does not indicate that the reaction is first order with respect to nitrogen dioxide. In fact under certain conditions lowering the pressure of nitrogen dioxide will cause an increase in reaction rate. This, upon consideration, would seem to indicate that the process of diffusion of some molecules through the gas phase plays an important part. The nuclei on the surface may well be, therefore, minute amounts of oxide formed by the reaction of mercury vapor with nitrogen dioxide or removed from the walls by the rush of incoming gas. That the latter effect is important is indicated by the gradual acceleration of the reaction with use of the reaction vessel.

II. Experimental

A. A Study of the Thermal Reaction

1. Effect of Length of Use of the Reaction Vessel on the Rate of Reaction.—After a lengthy consideration of the possible ways of measur-

[5] Gibson and Noyes, THIS JOURNAL, **43**, 1255 (1921).

ing the rate of reaction between mercury and nitrogen dioxide, it was decided to adopt the technique used in the previous investigation.[1] This consists in admitting the nitrogen dioxide and in observing the time of formation of a solid film on the surface. This method leaves something to be desired in a quantitative sense, but the rate of reaction may be considered to vary inversely with the time of formation of the film.

In the earlier experiments[1] only one reaction vessel was used. The times of formation of the film were found to be very reproducible over short intervals of time, providing the nitrogen dioxide was carefully dried. A reduction in the pressure of the nitrogen dioxide caused a slight increase in the time of formation of the film.

In the present experiments, certain reaction vessels gave values of the time of formation of the film (t_0) which were in good agreement with previous values. However, many reaction vessels gave times of formation which differed by more than the experimental error from the values previously reported. In general, the values of t_0 decreased with use of a given reaction vessel. Table I shows values of t_0 for a certain reaction vessel.

TABLE I

EFFECT OF LENGTH OF USE ON THE TIME OF FORMATION OF A SOLID FILM

Run numbers	1–18	19–36	37–46	47–53[a]
t_0 (av.) secs.	48	38	24	37

[a] Cell cleaned before making these runs.

2. Effect of the Shape of the Reaction Vessel on the Rate of Reaction.—It became clear early in this work that some factors were present and caused variation in the values of t_0 and which were not of obvious importance. Factors which, at first glance, would seem to be of importance are: radiation, temperature, purity of the mercury and purity of the nitrogen dioxide. There seemed, however, to be a great variation between various reaction vessels. Table II illustrates the point in question. The two reaction vessels were sealed together so that the same pressure of nitrogen dioxide was introduced into the two vessels at the same time. The mercury used was from the same source.

TABLE II

VARIATION OF t_0 WITH REACTION VESSEL

Run numbers	3–8	14–18
t_0 (av.) secs. I	34	23
t_0 (av.) secs. II	55	33

Many different reaction vessels were used in these experiments and many changes in design were made. As a result of all of the observations made, the following statements seem justified: the values of t_0 do not depend in any obvious manner on the ratio of surface to volume in the reaction vessel. While less accuracy was possible with small surfaces of

mercury than with large, the value of t_0 does not depend primarily on the surface. The only factor of importance in this connection we were able to discover was in the relation of the entrance of the gas to the mercury surface. If the inlet was so placed that any dust particles or impurities from the wall would be carried to the surface of the mercury, the rate of reaction seemed to be rapid. Reaction vessels with the well containing the mercury large compared to the diameter of the vessel seemed to exhibit abnormally fast reactions. In cells of this type any impurity removed from the walls by the rush of incoming gas would be sure to impinge upon the surface.

3. **Effect of Moisture on the Values of t_0.**—A vessel which had shown an average value of t_0 with dry nitrogen dioxide of forty-three seconds, was filled with water vapor at a pressure of 5 mm. prior to admitting the nitrogen dioxide. The value of t_0 then became twenty seconds and remained short for several runs.

4. **Effect of Temperature on the Values of t_0.**—Most of the experiments reported in this article were carried out at room temperature. Minor variations in temperature did not seem to produce a marked change in the values of t_0. One vessel which showed an average value of t_0 of forty-five seconds at a temperature of 23° showed a value of sixty seconds at a temperature of 2°.

5. **Effect of Pressure on the Values of t_0.**—In the previous work[1] it was found that the time of formation of the film increased with reduction in pressure of the nitrogen dioxide. The change was not very great, an increase in time from seventy to one hundred seconds being noted as the pressure fell from 400 mm. to 40 mm. Phenomena similar to those previously reported could be obtained when the reaction vessel had been freshly cleaned and the values of t_0 were of the same order as those previously reported. However, after the reaction vessel had been used for some time and the time had become appreciably shorter than those previously reported, a reduction in pressure led to a reduction in time of formation of the film until very low pressures had been reached. Very low pressures invariably led to an increase in the values of t_0. However, it was observed that the thickness of the film was considerably greater for high pressures than for low pressures. Table III shows data illustrating this point.

TABLE III

EFFECT OF PRESSURE ON THE VALUES OF t_0

(T = 25°)

Run no.	1	2	3	4	5	6	7
Press. of NO_2, cm.	46	30	26	17	10	5	2
t_0, seconds	43	47	48	42	46	28	34

At lower pressures t_0 became as long as three minutes or more. Runs 1 to 5 agree within experimental error.

6. **Effect of Foreign Gases on the Values of t_0.**—After each run the reaction vessel was flushed out with either nitrogen or hydrogen which had been dried by passage through phosphorus pentoxide. The system was then evacuated to a pressure below a tenth of a millimeter before admitting the nitrogen dioxide. No difference in behavior was noticed between cells flushed with hydrogen and those flushed with nitrogen. In order to determine the effect of foreign gases, nitrogen and oxygen were mixed at different times with the nitrogen dioxide before admitting it to the reaction vessel. The time of formation of the film seemed to be independent of the pressure of foreign gas at constant pressure of nitrogen dioxide. This point is shown in Table IV.

TABLE IV

EFFECT OF FOREIGN GASES ON THE VALUE OF t_0 ($T = 25°$)

Number of runs	Press. of NO_2, cm.	Foreign gas	Press. of foreign gas, cm.	t_0 secs.
4	24	..	..	42
4	24	O_2	24	42
4	24	N_2	24	44

B. Attempts to Accelerate the Reaction by Various Means.

1. **The Effect of Radiation.**—An attempt was not made to repeat all of the previous work on the acceleration of the reaction by radiation. The effect of radiation shown in the previous work[1] could be duplicated if the reaction vessel was clean, that is, before the value of t_0 had become very short. Accelerating and retarding potentials produced about the same effect as those found previously. For example, a vessel which showed a value of t_0 of eighty-eight seconds (average of twelve determinations) showed a time of formation of the film under the influence of radiation from a quartz mercury arc lamp of sixty-five seconds (average of sixteen determinations) when small accelerating potentials were used. However, the behavior of the reaction was much more erratic than was found previously. Great care in drying the nitrogen dioxide, changing the type of stopcock grease and even rebuilding the entire apparatus to eliminate possible impurities did not produce any distinct improvement in the reproducibility of the results. Some factor which we were unable to discover caused variations in the results. However, there is no reason to doubt the previous work and the effect of radiation can be duplicated under proper conditions.

As shown in the preliminary discussion, the effect of radiation may be open to a variety of interpretations, so that it was thought desirable to carry out a series of experiments which would permit a decision as to the relative merits of the various hypotheses.

2. **Effect of a High Potential Discharge.**—The reaction vessel was thoroughly swept out with either dry nitrogen or dry hydrogen and then

pumped out to a pressure of about a tenth of a millimeter. A discharge was started, either with a spark coil or with a $^1/_4$ kw. transformer. Small amounts of residual gas would frequently cause a film of oxide to form on the surface. The surface was always renewed before admission of the nitrogen dioxide. The admission of the nitrogen dioxide stopped the discharge due to its relatively high pressure. However, the gas is admitted into a space plentifully supplied with ions (and radiation), certainly a far higher concentration than was ever obtained by the photoelectric effect. Several possibilities may now be discussed. 1. In some experiments the discharge was passed between the mercury and an electrode placed above the surface. 2. In other experiments the discharge was passed between two electrodes placed in the tube through which the nitrogen dioxide passed in entering the reaction vessel. Varying low potentials were imposed between the mercury and an electrode placed above the surface of the mercury at a distance of about one and a half centimeters. Table V presents a summary of data obtained with one reaction vessel.

TABLE V

EFFECT OF DISCHARGE ON THE VALUES OF t_0

Number of runs	Pressure of NO_2, cm.	t_0, secs., av.	Remarks
..	17–20	180–300	Hg one electrode. Light, uniform film formed instantly. Heavy film very slow in forming
10	17–20	54	No discharge
6	17–20	43	Discharge in entrance tube. Potentials on Hg with ref. to electrode above surface of −35 to +35 volts produced no regular effect
8	17–20	61	No discharge
27	17–20	39	Discharge in entrance tube

3. Effect of Electrons Emitted by Radiation from a Platinum Electrode Placed Above the Mercury Surface.—A few experiments were tried in which the nitrogen dioxide entered the reaction vessel in such a manner that it passed in front of a platinum plate on which radiation from a quartz mercury arc lamp was incident. No acceleration of the reaction was observed although the photoelectric current was so small that no decided effect would have been expected.

4. Effect of a Beam of Cathode Rays.—One reaction vessel was arranged in such a way that an electron beam formed in a low pressure discharge in hydrogen (with heated cathode) was directed into the space directly above the mercury surface. The beam could be deflected toward or away from the mercury surface by varying the potential between the mercury surface and an electrode placed above the surface. No definite acceleration was noted.

5. Effect of Strong Radiation (not Incident on the Mercury Surface).—

It has been shown by Norrish[6] that nitrogen dioxide decomposes under the influence of radiation. It is possible that the nitrogen dioxide might be activated by the radiation which it absorbs and react more rapidly than normally with mercury. However, radiation in the visible and near ultraviolet regions was found to be without effect. This agrees with previous observations.[1]

An attempt was also made to accelerate the reaction between nitrogen dioxide and hydrogen by radiation. Norrish[6] had found that hydrogen produced little effect on the pressure increase when nitrogen dioxide was illuminated by radiation from a quartz mercury arc lamp. This observation has been confirmed for the three regions of the spectrum, (*a*) visible, (*b*) to the limit of transmission of quartz and (*c*) through fluorite, using a condensed discharge through hydrogen.[7] A discharge through the hydrogen–nitrogen dioxide mixture caused an explosion. This indicates, presumably, that activation of nitrogen dioxide is in itself not sufficient to cause reaction with hydrogen. This evidence, coupled with the lack of effect of visible radiation on the rate of reaction of nitrogen dioxide with mercury, indicates that activated nitrogen dioxide molecules are not appreciably more reactive chemically than normal molecules toward mercury and hydrogen.

6. Effect of Electrons Emitted by Thermal Means from a Filament Placed Above the Surface.—A few experiments were made in which a heated filament was placed in the reaction vessel above the mercury surface. A high vacuum was attained before the admission of the nitrogen dioxide. Table VI shows results obtained in this manner with one reaction vessel.

TABLE VI

EFFECT OF ELECTRON EMISSION FROM FILAMENT

Pressure of nitrogen dioxide, 7–10 cm.; $T = 25°$

Number of runs	t_0, av.	Remarks
12	45	No filament
30	46	Filament on. Potential between filament and Hg surface varied from +6 to −6 volts

The thermoelectric currents observed in these experiments were far greater than the photoelectric currents observed in paragraph 1.

III. Discussion of Results and Conclusions

From the results on the thermal reaction, it is obvious that the time of formation of the film is not solely a function of the pressure of the nitrogen dioxide, the temperature and the purity of the mercury. Indeed, it

[6] Norrish, *J. Chem. Soc.*, **1927**, 761. See also Dickinson and Baxter, THIS JOURNAL, **50**, 774 (1928).

[7] Kassel and Noyes, THIS JOURNAL, **49**, 2495 (1927).

seems that some factor which depends on the geometry of the reaction vessel must be taken into account. The authors are inclined to the conclusion that impurities may be removed from the walls by the incoming gas and that these impurities, if carried to the mercury surface, may catalyze the reaction. The impurities would seem to be mainly mercuric oxide. This hypothesis satisfactorily explains the decrease in the values of t_0 with increased use of the cell. Also, we may have here an explanation of the peculiar effect of pressure. Indeed one may derive an equation which fits the data reasonably well by assuming that two effects are to be considered, one dependent on the pressure of the nitrogen dioxide directly and the other a diffusion process involving some impurity which must diffuse through the gas. The diffusion would be more rapid at low pressures and only at exceedingly low pressures would the values of t_0 increase markedly. The phenomena are doubtless very complex and it is entirely possible that other effects due to stopcock grease and to spurious charges induced by the rush of gas must be considered. However, the authors are inclined to the belief that the above explanation will account for many of the facts observed.

When attention is turned to an explanation of the various attempts to accelerate the reaction, the following facts seem to be proved. The presence of ions in the gas (nitrogen or hydrogen) in the reaction vessel at the time the nitrogen dioxide is admitted will cause an increase in the rate of reaction between nitrogen dioxide and mercury. In the case of some of the extremely long times observed when the discharge method was used, it is obvious that there is a very rapid reaction which caused a uniform film, exceedingly thin, to be formed on the surface and that this film acts as a protective coating. With the discharge in the entrance tube so that the mercury did not serve as one electrode, the film seemed to be normal in character but formed more rapidly than in the absence of discharge. These facts indicate that the presence of ions will cause an increase in the rate of reaction between mercury and nitrogen dioxide. However, the presence of small numbers of ions (comparable to the number given off due to the photoelectric effect or somewhat larger) is without effect that can be detected. Activation of the nitrogen dioxide by radiation is also without effect. There is no evidence to indicate that negative ions produce more effect than positive ions.

The effect of the light announced in the previous article[1] and confirmed in the present investigation must, therefore, be associated with the activation of a surface layer of gas (or perhaps of mercury). This activation seems to be associated in some way with the photoelectric effect.

As a general conclusion we may state that the thermal reaction between mercury and nitrogen dioxide depends on conditions which vary with the geometry and cleanliness of the reaction vessel. The rate (as determined

by the formation of a surface film) is accelerated by the presence of relatively large numbers of ions in the gas at the time it is admitted. There may, however, be a rapid reaction uniform over the surface which will hinder the formation of a heavy film. Evidence indicates that positive and negative ions are equally effective in producing acceleration of the reaction. The action of light is best ascribed to the activation of a surface film on the mercury, perhaps adsorbed gas or a small amount of oxide, which is associated with the photoelectric emission. Numbers of ions in the gas comparable to the number produced by the photoelectric effect do not produce noticeable changes in the time of formation of heavy films. This view is more in accord with the views first expressed,[1] but the phenomena are shown to be more complicated than had been supposed. Acceleration due to radiation is not observed when the reaction vessel has become dirty and the dark reaction has become very fast.

Summary

1. The rate of reaction between mercury and nitrogen dioxide as measured by the time of formation of a uniform visible film is dependent, among other things, on the shape of the reaction vessel. The times tend to become short as the reaction vessel is used. There are variable factors which have not been entirely determined.

2. The reaction is accelerated by the presence of large numbers of ions. Positive and negative ions, as far as can be determined, have equal effects.

3. The action of light in accelerating the reaction is most probably to be ascribed to the activation of a surface film. This seems in some way to be associated with the photoelectric effect.

4. Acceleration of the dark reaction with continued use of the vessel may be due to the contamination of the surface by minute crystals swept in by the nitrogen dioxide. This acceleration may obscure the action of the light.

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