

QuasiUnimolecular and QuasiBimolecular Steps in Complex Reactions. The Dissociation of Nitrogen Pentoxide

Richard A. Ogg Jr.

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"... attempt to develop a mixed catalyst with an outstanding activity has been a failure." This failure however is not due to an absence of correlation between activated adsorption and conductive characteristics of the adsorbent but to a deceptive choice of the operative parameter. Volkenshtein² has shown that the main features of activated adsorption (activation energy, isotherms, differential adsorption heats decreasing with coverage) can be obtained with an energetically homogeneous but temperature sensitive surface. Active centers may be originally present but new ones are produced either on filling up at constant temperature or by a temperature increase, at the expense of an energy E which appears as an activation energy in the rate equation for adsorption. In certain cases, we may identify E with the energy ϵ necessary to send a bound electron into the conduction band. Details will be described elsewhere. Let it be said only that such an activation throws much light on some facts which were obscure from the standpoint of the usual theories. Since 1932, Taylor³ has repeatedly emphasized that the observed adsorption rates were not compatible with the assumption that every molecule hitting the surface with the necessary activation energy is adsorbed. Pace and Taylor,⁴ reporting that the adsorption rates for H_2 and D_2 on Cr_2O_3 and $ZnO-Cr_2O_3$ are identical, suggested that "the activation energy of the adsorption process is required by the solid adsorbent." This activation of the solid has also been considered by Hedvall⁵ whose concepts have been examined by Möglich.⁶

Assuming that the concentration of quasi-free electrons is rate determining, Wagner concludes that 1 percent Ga_2O_3 has no influence on the reaction velocity and he defines active centers of a special nature. No such restrictive hypothesis is needed if absolute values of K (specific conductivity) are of little interest but if ϵ has to be measured and appreciated as the determining parameter. There is a relationship between K and ϵ (Meyer's "straight line") but from the data which led Meyer to his systematization and from their analysis by Gisolf,⁷ it can be seen that large differences in conductivities do not entail a large difference $\Delta\epsilon$ between the corresponding values of ϵ ; $\Delta\epsilon$ actually depends on changes in concentrations of both defects and electron traps and can be quite small. If it were 1350 cal. mole⁻¹, the reaction rates would differ at 725°C by a factor of two only.

We thus think that Wagner underestimated the scope of his own work. Further attempts to correlate adsorption and catalysis with semiconductivity ought to include measurements of both K and ϵ .⁸ We wish to express our indebtedness to Professor H. S. Taylor who suggested a large number of the ideas contained in this note.

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² F. F. Volkenshtein, Zeits. f. Khim. 23, 917 (1949).

³ H. S. Taylor, Trans. Faraday Soc. 28, 137 (1932).

⁴ J. Pace and H. S. Taylor, J. Chem. Phys. 2, 578 (1934).

⁵ J. A. Hedvall, Zeits. f. angew. Chemie 54, 505 (1941).

⁶ F. Möglich and R. Rompe, Physik. Zeits. 44, 77 (1943).

⁷ J. H. Gisolf, Ann. d. Physik 1, 3 (1947).

⁸ Bevan, Shelton, and Anderson, J. Chem. Soc. 1729 (1948).

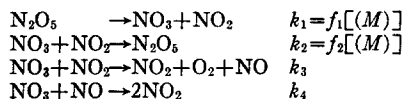
Quasi-Unimolecular and Quasi-Bimolecular Steps in Complex Reactions. The Dissociation of Nitrogen Pentoxide

RICHARD A. OGG, JR.*

Mallinckrodt Chemical Laboratory, Harvard University,
Cambridge, Massachusetts

February 15, 1950

THE mechanism previously proposed¹ for the decomposition of N_2O_5 entails a hitherto unemphasized prediction of an apparent "falling off" of the first-order rate constant at *extreme low pressure*. In the reformulation below, the symbol M denotes the molecular species responsible for collisional activation and deactivation.



(The rate constant for step 4, not comprised in the original formulation, does not appear in the rate expression for the decomposition. It is required to explain the kinetics of the reaction between N_2O_5 and added NO.) The various detailed theories² of quasi-unimolecular reactions allow derivation (on the basis of assumed molecular models) of specific mathematical forms for the function f_1 . Inasmuch as k_1/k_2 is an equilibrium constant, f_1 and f_2 are identical in form, in the sense that $f_1[(M)_A]/f_1[(M)_B] = f_2[(M)_A]/f_2[(M)_B]$. The various theories converge in the region of extreme low pressure—i.e., as $(M) \rightarrow 0$, $k_1 \rightarrow k_{act}(M)$, where k_{act} is the collisional activation constant.

The following rate expression results for the decomposition.

$$-\frac{d(N_2O_5)}{dt} = k_{ex}(N_2O_5) = \frac{2k_1k_3}{k_2 + 2k_3}(N_2O_5).$$

As previously shown, when $(M) \rightarrow \infty$, $k_2 \gg 2k_3$ and hence

$$k_{ex, \infty} = \frac{2k_1k_3}{k_2}.$$

At all values of (M)

$$\frac{1}{k_{ex}} = \frac{k_2}{2k_1k_3} + \frac{1}{k_1} = \frac{1}{k_{ex, \infty}} + \frac{1}{k_1}.$$

As $(M) \rightarrow 0$, $k_1 \rightarrow k_{act}(M)$,

$$\frac{1}{k_{ex, 0}} \rightarrow \frac{1}{k_{ex, \infty}} + \frac{1}{k_{act}(M)}.$$

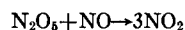
The above conclusion as to eventual falling off of k_{ex} is strikingly confirmed by the studies of Linhorst and Hodges³ performed at pressures of the order of 10^{-3} mm Hg. Their empirical equation is of exactly the above linear form. From their data at various temperatures, for M simply N_2O_5 itself, the collisional activation rate constant

$$k_{act} = 10^{18.9} e^{-\frac{18,300}{RT}} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}.$$

The activation energy of step 1 at high pressures cannot be less in absolute value than the energy change associated with this process. From the previous estimate¹ a value of about 21.6 kcal./mole seems very probable for this activation energy. It is seen above that the limiting value at extreme low pressures is some 18.3 kcal./mole. In the Kassel² classical model based theory, this difference is merely $(s-3/2)RT$, where s is the effective number of classical oscillators. Noting that these figures apply to some 300°K, the corresponding value for s is about 7. This is entirely reasonable in view of the maximum possible value of 15 for N_2O_5 . Using $s=7$, the above frequency factor leads to a collisional deactivation rate constant of some 10^{16} mole⁻¹ cm³ sec⁻¹. The collision diameter corresponding to this figure is in sensible agreement with the viscosity studies on N_2O_5 .⁴

The above estimated activation energy and a "normal" frequency factor lead to an expected limiting high pressure value of k_1 at 300°K of the order of magnitude of 10^{-1} sec⁻¹. From the above estimate of s the classical theory of Kassel² predicts that N_2O_5 pressures of the order of hundreds of millimeters of Hg would be necessary to reach *one-half* of the limiting high pressure value of k_1 . Thus step 1, when studied separately, is expected to show very marked falling off of rate constant at moderate pressures, and should be markedly accelerated by addition of chemically indifferent gases.

The work of Smith and Daniels⁵ on the kinetics of the reaction



offers one approach to study of the rate of step 1. Neglecting step 3 the resulting rate expression is

$$-\frac{d(NO)}{dt} = \frac{k_1(N_2O_5)}{1 + [k_2(NO_2)/k_4(NO)]}.$$

The reaction was observed to be zero order with respect to NO, but no marked inhibitory effect of NO_2 was found. At the relatively very low pressures used, the value of k_2 has apparently

fallen off so much that $k_2 \ll k_4$. The first-order constants show a systematic trend with increase of pressure, suggesting the above predicted quasi-unimolecular behavior. It is to be expected that addition of chemically indifferent gases, such as CO_2 and SF_6 , would greatly accelerate the reaction.

* Currently on leave from Stanford University, California.

¹ R. A. Ogg, Jr., *J. Chem. Phys.* **15**, 613 (1947).

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⁵ J. H. Smith and F. Daniels, *J. Am. Chem. Soc.* **69**, 1735 (1947).

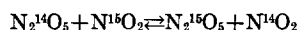
Experimental Evidence for the Quasi-Unimolecular Dissociation of Nitrogen Pentoxide

RICHARD A. OGG, JR.,* WILLIAM S. RICHARDSON, AND M. KENT WILSON
Mallinckrodt Chemical Laboratory, Harvard University,
Cambridge, Massachusetts
February 15, 1950

REACTION rate studies involving nitrogen pentoxide have been carried out, concentrations of respective components being determined by intensity measurements on suitable infra-red absorption bands. Use was made of the double beam recording spectrophotometer Model B manufactured by Baird Associates. Absorption cells were of Pyrex glass tubing 4.5 cm long and 4.0 cm in diameter, fitted with interchangeable windows or rocksalt, silver chloride or fluorite. Of the "strong" bands of N_2O_5 between 2 and 16μ , only that at approximately 1350 cm^{-1} is clearly resolved from strong bands of N_2O_4 . For the isotopic nitrogen exchange studies, use was made of the very strong ν_3 fundamental of NO_2 at 1621 cm^{-1} . The appearance of the band envelope proved particularly sensitive to pressure broadening caused by admixture of foreign gases, the *P* and *R* branches showing an apparent intensity increase much greater than that of the *Q* branch. When NO_2 was prepared (by heating with PbO) from KNO_3 containing 57 atomic percent of N^{15} , the resulting additional spectrum displayed the expected isotope displacement to longer wavelength, amounting to about 40 cm^{-1} . In the presence of considerable foreign gas the *P* branch of N^{15}O_2 is clearly resolved, and its intensity is a satisfactory concentration index. Concomitantly in such an isotopic mixture, the intensity of the *R* branch of N^{14}O_2 may be used to measure the concentration of this species.

N^{15} enriched N_2O_5 was prepared by ozonization of enriched NO_2 . After separation from oxygen and ozone, it was vaporized into the evacuated absorption cell. After tracing the relevant region of the spectrum, the spectrophotometer was stopped at the maximum of the *P* branch of N^{15}O_2 . Opening a stopcock to an attached bulb caused admission of a mixture of CO_2 and isotopically normal NO_2 . The transmission scale was read at measured time intervals, the change corresponding to production of N^{15}O_2 . When exchange equilibrium was reached, the entire spectrum was traced, the intensities of the N_2O_5 , NO_2 , and CO_2 bands yielding the composition of the reaction mixture. (Concentration-intensity relations had been determined empirically.) In typical experiments the respective partial pressure ranges for these three components were some 5–25, 10–50, and 50–500 mm Hg. Experiments were also performed in which isotopically normal N_2O_5 was admitted to the cell containing enriched NO_2 . These latter showed qualitatively the rapid exchange, but for rather apparent reasons are not well suited to accurate measure of the rate.

The above studies show the equilibrium



to be established very rapidly, the rate being apparently first order with respect to N_2O_5 and zero order with respect to NO_2 (although greater precision is required to establish these orders exactly). This indicates that at least the major rate determining step is the dissociation



At 27°C the rate constant of this step is of the order of magnitude of 0.5 sec^{-1} when the partial pressure of CO_2 is 500 mm Hg. Decrease of CO_2 concentration markedly decreases the rate, the above velocity constant decreasing by a factor of about five when the CO_2 partial pressure is reduced tenfold. It appears that still higher pressures would be required to attain the limiting value of the rate constant. It is to be noted that this behavior qualitatively substantiates the prediction of quasi-unimolecular behavior with "falling off" at relatively high pressures.¹ Probably the principal value at this stage of the studies is the first experimental demonstration of the expected isotopic exchange reaction in the gas phase. The previous studies² with N^{15} were confined to solutions in CCl_4 , and gave an even rougher indication of the magnitudes of the rates.

Rate studies of the reaction



were carried out at 27°C by following the disappearance of N_2O_5 . The cell initially contained pure N_2O_5 vapor at some 40 mm Hg pressure, and the spectrophotometer was set at the maximum of the 1350 cm^{-1} band. After admission of an $\text{NO}-\text{CO}_2$ mixture, the procedure was as above. (The characteristic NO fundamental does not overlap other bands of interest.) Initial concentrations of NO varied from some 60 to 200 mm Hg, and that of CO_2 from 50 to 500 mm Hg. The NO_2 formed by the reaction proved to have a marked inhibiting effect, which was quantitatively greater, the higher the concentration of CO_2 . As nearly as could be judged from the experiments, this inhibition is in agreement with the form of the rate expression given by the proposed mechanism.¹ Initial rates were determined by extrapolation, and proved to be zero order with respect to NO , and first order with respect to N_2O_5 . At a partial pressure of CO_2 of 500 mm Hg, the first-order rate constant is within experimental uncertainty identical with that found from the isotope exchange. Decrease of CO_2 concentration produced a marked decrease of the initial rate constant—again in a fashion indistinguishable from that of the isotope exchange reaction. To be sure, the relatively low precision of both sets of measurements does not warrant more than the statement that it seems highly probable that the same rate determining step must be common to both reactions. Further evidence for the correctness of the proposed mechanism is found in the experimental observation of the increase of the inhibitory effect of NO_2 with increasing CO_2 concentration—an effect to be expected from the necessarily quasi-bimolecular character of the association reaction $\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$.

Current continuation of both sets of studies is aimed at improvement of precision, and the extension to other temperatures, as well as the use of various chemically indifferent gases. These studies hold promise of completion of the first body of experimental evidence adequate for comparison with the refined theories of quasi-unimolecular reactions.

* Currently on leave from Stanford University, California.

¹ R. A. Ogg, Jr., *J. Chem. Phys.* **18**, 572 (1950).

² R. A. Ogg, Jr., *J. Chem. Phys.* **15**, 613 (1947).

The Behavior of Glass Electrodes in Acid Solutions

MALCOLM DOLE
Department of Chemistry, Northwestern University, Evanston, Illinois
February 24, 1950

UNDER the above title, Sinclair and Martell¹ have recently published a description of a study of glass electrodes which they have made in concentrated hydrochloric and sulfuric acid solutions. In their paper they state, "In view of the experimental results presented in this paper in comparison with the results predicted by Dole's theory of the negative errors, it is to be concluded that the assumption of water transport through the glass membrane does not satisfactorily account for the negative errors of the glass electrode. It would seem, therefore, that the only remaining possibility of accounting for these deviations would be to attribute them to anions."