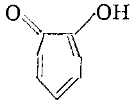
is very similar to tropolone



which might be considered the enol form of an α-diketone.

If the salicylaldehyde derivatives, containing a "true" carbonyl group and a phenolic hydroxyl group are considered, it is seen from previous work[6] that they form complexes of markedly lower stability than the tropolone complexes. In both cases, however, the size of the chelate ring formed is different from that of the tropolone complexes. This would seem to be another instance of the greater stability of a five-membered chelate ring over a six-membered one.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF NOTRE DAME]

A Study of the Kinetics of the Reaction between Nitrogen Dioxide and Alcohols

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The reaction $2NO_2 + ROH = HNO_3 + RONO$ has been studied photometrically at pressures from one to ten mm., in apparatus having a small surface to volume ratio. Initially the forward rate is given by the expression: $dp_{NO_2}/dt = k \cdot (p_{NO_2})^2(p_{ROH})$. The constant k and the equilibrium constant at 25° have been evaluated for five of the lower paraffin alcohols. For any given batch run, values of "k" computed from the above equation were found to increase with extent of reaction indicating an autocatalytic effect. Meager temperature data on methanol indicate a negative temperature coefficient for the reaction as given above. A mechanism involving a simple reaction and a concurrent catalytic reaction dependent on a trace secondary product or on surface effects are tentatively postulated.

The reaction between nitrogen dioxide and methanol was observed by Harris and Siegel,[1] a decolorization being noted. Recent work by Yoffe and Gray[2] identified the products of this reaction spectroscopically as nitric acid and nitrite ester. No literature has been heretofore reported in which an attempt was made to quantitatively evaluate the rate laws governing the reaction.

The reaction of NO_2 with alcohols is of interest as a rapid, third-order reaction with an apparent negative temperature coefficient. It is of further interest in elucidation of the mechanism by which the oxides and acids of nitrogen react with alcohols. Practically, the reaction provides a simple way of making nitrites.

This paper describes a method and apparatus devised for the measurement of a rapid gas phase reaction between nitrogen dioxide and methanol, ethanol, *n*-propanol, isopropyl alcohol and *t*-butyl alcohol, at partial pressures of 0.5 to 5.0 mm. for each reactant. Data were taken at 25° for all alcohols investigated, and also at 0 and 15° for methanol. The kinetics of the reaction are discussed and a possible mechanism tentatively suggested.

Experimental

The reaction between NO_2 and alcohols is particularly well suited to a colorimetric method for following its progress. With the green light used (450–600 mμ) it was experimentally determined that partial pressures of other materials than NO_2 in considerable excess of maximum values expected had no detectable effect on light absorption. NO_2 is intensely colored and was detectable to well below 0.1 mm.

Apparatus.—Two reaction cells were used in the course of these experiments, both being cylindrical in shape and of length 122 cm., but having volumes of 1870 and 18,500 cc. The smaller tube was equipped with optically flat sealed-in Pyrex windows, while the larger was sealed at the ends with plate glass affixed with gasket sealing compound. Diffusion calculations confirm experimental findings that these surfaces have no detectable effect on the reaction. Likewise stopcocks used in the apparatus were experimentally found to have no effect on the reaction, or on reactants stored adjacent to the stopcocks. Shape and construction of the apparatus made thermostatic control through making the whole small laboratory in which the data were taken into an isothermal room imperative. Temperature control could be maintained at 25 ± $^1/_2$°, a temperature fluctuation introducing a maximum error of 4% in rates observed. Initial reactant pressures had to be kept of the order of several mm. in order that the reaction rate would remain measurable. Precise measurement of amounts used was obtained by letting considerable pressures into calibrated bulbs where the pressures could be evaluated with a manometer at the temperature of the thermo-room. At the beginning of a run, the amount taken was flashed into the reaction cell (evacuated to 0.05 mm.), where the final pressure could be estimated from the knowledge of the volumes involved. In measuring NO_2, due account was taken of the NO_2, N_2O_4 equilibrium.

The progress of the reaction was followed by determining the light absorption caused by the NO_2 present. Light from an unfrosted incandescent bulb was passed through a $CuCl_2$–$CaCl_2$ filter which removed wave lengths photochemically decomposing to NO_2. The spherical flask containing the filter solution was found to act as a lens furnishing an adequately focused parallel light beam. This beam was split into two beams through the use of offset plane mirrors which reflected the light through the reaction cell and through a blank tube used for standardizing intensity measurements. More plane mirrors and a shutter were used to cause the light beam desired to impinge on a photronic photocell. This activated a sensitive galvanometer whose readings were recorded.

Materials.—Nitrogen dioxide was used directly from lecture bottles supplied by the Matheson Co. Analysis showed this to contain less than 0.5% N_2, O_2, etc. The chemical nature of NO_2 precludes the presence of moisture, while the metallic container precludes the existence of all but traces of nitric acid in NO_2 used. Propanols and butanol used were dried over calcium carbide and distilled. Methanol and ethanol were used as C.P. grade reagents after tests indicated that rate deviations due to water present in reagent grade chemicals were at most 3%.

Method.—The reaction tubes were evacuated to 0.05 mm. (McLeod gage), flushed with air, and re-evacuated.

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[1] L. Harris and B. M. Siegel, THIS JOURNAL, **65**, 2520 (1947).

[2] A. D. Yoffe and Peter Gray, *J. Chem. Soc.*, 1412 (1951).

TABLE I

Equilibrium and Initial Rate Constants (K in mm.$^{-1}$), (k_o in mm.$^{-2}$ min.$^{-1}$), temp., 25°.

Initial				Initial				Initial				Initial				Initial			
NO_2	Alc	K_{eq}	k_o	NO_2	Alc	K_{eq}	k_o	NO_2	Alc	K_{eq}	k_o	NO_2	Alc	K_{eq}	k_o	NO_2	Alc	K_{eq}	k_o
Methanol				Ethanol				*n*-Propanol				Isopropyl alcohol				*t*-Butyl alcohol			
3.00	0.84	2.33	0.040	3.10	0.83	0.78	0.049	3.00	0.50	0.60	0.059	2.80	2.52	0.36	0.034	3.00	2.00	0.039	0.0155
3.20	1.61	2.58	.032	3.03	1.32	.76	.038	3.00	1.00	1.30	.061	3.03	1.32	.32	.039	3.00	1.50	.046	.0185
3.00	2.82	1.76	.030	3.00	1.86	.69	.035	3.00	1.50	0.59	.052	3.10	0.82	.28	.033	3.00	2.51	.054	.014
3.00	3.83	1.82	.027	3.00	2.92	.77	.034	2.76	2.00	0.81	.046	2.75	.4	.28	.033	3.03	1.00	.040	.0155
3.00	4.86	1.88	.024	3.03	3.30	1.20	.037	4.80	1.94	1.6	.065	4.92	1.70	.20	.025	3.00	0.50	.057	.018
1.00	2.94	2.04	.031	1.05	3.06	1.07	.033	3.76	2.00	1.3	.056	3.76	1.76	.24	.029	0.86	2.00	.094	.015
2.00	2.88	0.85	.028	2.14	3.00	0.92	.033	2.02	2.00	1.2	.055	1.99	1.88	.20	.029	1.85	2.00	.076	.014
4.00	2.75	1.60	.022	4.00	2.88	.69	.028	0.96	2.00	1.0	.060	3.00	1.80	.32	.028	4.00	2.00	.065	.014
5.00	2.69	1.26	.028	5.00	2.82	.72	.030	Av.		1.06	.057	0.96	1.94	.19	.030	Av.		.059	.015
Av.		1.8	.029	Av.		.86	.035					Av.		.27	.031				

Evacuated measurement bulbs were then filled to desired pressures with reagents taken from Pyrex storage bulbs (NO_2 as vapor, alcohol as liquid at its vapor pressure). Light intensity through the evacuated tube was adjusted to a suitable value with the rheostat and checked with standard intensity tube. Exactly on the even minute of a running stopwatch, stopcocks admitting reactants to the measurement cell were opened rapidly. Galvanometer readings were then taken at suitable intervals. Timing errors were not greater than small fractions of a second, and mixing errors by this manner of operation were found to be unobservable (mechanical agitation with a glass circulation pump indicated identical data to that taken without agitation). Standard intensity and the temperature of the thermoroom were checked frequently.

Galvanometer readings were translated into pressures of NO_2 present by means of an empirically determined calibration curve for the system and instruments.

Thus data relating pressure of NO_2 and time were determined. These data were plotted on Cartesian coördinate paper, and the rates at divers values of extent of reaction were determined by taking the slopes to these pressure–time curves. Data were taken holding the partial pressure of one reagent constant and varying the other over a considerable range, for both reactants. Thus initial dependance of rate could be determined for both reactants, in each case all variables except the one investigated were constant. These data (rate *vs.* partial pressure of one reactant) were plotted on log log coördinate paper, the slope of the curve drawn indicating the "order" of the reaction with respect to the component investigated, and the intercept at unit partial pressure indicating a measure of the specific reaction rate constant. Runs were allowed to react until no change in NO_2 partial pressure could be detected in 20 minutes. This last reading was assumed to represent equilibrium.

Meager temperature data for methanol were taken by flashing measured amounts of reactant into a cooled auxiliary reaction flask. Reaction was allowed to proceed for a given time when the reaction mixture was flashed into the evacuated light absorption cell. From volume, temperature and measured NO_2 partial pressure data, the amount of NO_2 reacted could be evaluated. Each run produced only one point on the pressure–time curve. Temperature equilibrium was found to be very rapid, and the nature of the reaction rate laws governing the reaction enabled the almost complete stopping of the reaction with the three-fold pressure reduction involved in the measurement of NO_2 reacted.

Results

Using this apparatus and procedure, measurements have been made of the rate of reaction of nitrogen dioxide with methanol, ethanol, *n*-propanol, isopropyl alcohol and *t*-butyl alcohol. Initial rate measurements using divers partial pressures of reactants, indicate that for all alcohols used the rate depends on the second power of the NO_2 partial pressure and the first power of the alcohol partial pressure, with the specific rate constants of the order of 0.015 to 0.055 mm.$^{-2}$ min.$^{-1}$ (0.88 to 3.2 $\times$ 10^5 l.^{2}/mole^2 sec.). Attempts to correlate data taken after the reaction has produced product material using the rate law that holds initially failed badly. Rate "constants" calculated by this third-order law (after due correction had been made for the reverse reaction) showed a progressive increase as the reaction progressed to completion. This effect was noted for all alcohols used. A negative temperature coefficient was noted for methanol. Equilibrium constants at 25° were established.

Equilibrium and Stoichiometry.—For the reaction in the liquid phase, it has been definitely established that one mole of nitrite ester is formed for each two mole quantity of NO_2 added to the alcohol. Exact neutralization of the remaining solution after nitrite removal, with base, and subsequent evaporation to dryness yielded crystals melting within one degree of the melting point of the corresponding nitrate salt. Thus the over-all stoichiometry was indicated to be $2NO_2$ + alcohol = nitrite ester + nitric acid. That this stoichiometry holds in the vapor phase reaction is indicated by the spectroscopic analyses of Yoffe and Gray and by the equilibrium values taken in this Laboratory.

With the above stoichiometry, the ratio of NO_2 reacted to NO_2 remaining at equilibrium, squared, divided by the original alcohol present minus one half the NO_2 reacted, should be constant and equal to four times the equilibrium constant. Thus

$$K = (NO_{2o} - NO_{2eq})^2/4(NO_{2eq})^2(Alc_o - {}^1/_2(NO_{2o} - NO_{2eq}))$$

In all the runs made, equilibrium conversion was a very detectable quantity. The above expression for the equilibrium constant was the only one that gave reasonable correlations as to the "constancy" of the equilibrium constant. Thus while experimental error precluded precise estimation of "K," the values obtained adequately indicate that the reaction proceeds according to the same stoichiometry in the vapor phase as in the liquid phase.

Values of equilibrium constant computed and initial rate constant computed with third order mechanism with the corresponding initial partial pressures used are tabulated in Table I.

Initial Rate Data.—The third-order nature (with respect to NO_2 and alcohol) of the initial reaction shown by the constancy of the above given k_o values. That the reaction rate depends on the second power of the NO_2 partial pressure and the first power of the alcohol partial pressure is shown by rate *vs.* individual partial pressure plots with one concentration held constant on double logarithmic coördinate paper.

Rate Data after Initial Conditions.—After the reaction evolved some product material attempts were made to compute rate constants based on the third-order initial mechanism and the stoichiometry previously discussed. Such "constants" were found to progressively increase with increased extent of reaction. Typical results are shown in Table II, a run made with NO_2 and isopropyl alcohol with initial partial pressures of 3.75 and 1.70 mm., respectively. In fact, the pressure–time curves taken for very many of the runs made were very close to straight line functions, with rate being constant over considerable extents of reaction.

TABLE II

Initially charged, 3.75 NO_2, 1.70 isopropyl alcohol, 25°, $S/V = 0.3$ cm.$^{-1}$

NO_2 reacted	"k," mm.$^{-2}$ min.$^{-1}$	NO_2 reacted	"k," mm.$^{-2}$ min.$^{-1}$
0.00	0.030	1.00	0.088
.25	.037	1.25	.087
.50	.047	1.50	.106
.75	.065	1.75	.117

"Rate constants" for the secondary stages of the reaction were computed taking into account the reverse reaction. The "k" values were computed according to the equation

$$k = \frac{\text{Experimentally determined rate}}{(\mathrm{NO_2})^2(\mathrm{Alc_o} - {}^1/_2(\mathrm{NO_{2o}} - \mathrm{NO_2})) - (\mathrm{NO_{2o}} - \mathrm{NO_2})^2/4K_{\mathrm{eq}}}$$

Not only was it observed as a general phenomenon in all data taken that there was a progressive increase in "rate constant" as the reaction progressed to completion, but it was also observed that this trend was much more pronounced in the runs made with the lower initial amounts charged (lower initial rates). At the highest partial pressures used, the increase was scarcely noticeable, while at the lowest pressures the effect was so pronounced as to almost suggest that an induction period of low rate followed by increasing rates was present.

All possible mechanisms involving the products as autocatalytic agents failed to give any adequate correlations of the data. All data pointed to the conclusion that the catalytic effect observed was not only a function of the partial pressures of the divers reactants and products present, but also of the time required to achieve the partial pressures observed.

The time dependent nature of this "drift in the rate constant" can be explained in either of two ways: the first of these postulates the formation of a trace decomposition product of the primary products of reaction, nitrite ester and nitric acid; the second postulates that NO_2 adsorbed on the reactor wall acts as a catalyst and that the adsorption reaction is relatively slow with respect to over-all reaction rate.

The first of these mechanisms necessitates that the trace catalyst concentration is given by "X" = $\int_0^t k_d\,(\mathrm{HNO_3})^n\,dt$, and that the autocatalytic part of the rate will then be proportional to this concentration, "X." Since added nitrite has no effect on rate, it is assumed that this does not affect rate, gas phase or catalytic, except through the medium of the reverse reaction.

The second of these mechanisms indicates that the surface catalyst will be given by "X" = $\int_0^t k_a(s/V)(\mathrm{NO_2})dt$, and catalytic rate will then be proportional to this "concentration."

Both of these mechanisms were plotted to test the coincidence of experimental data with the theoretical curves predicted. Although there was a considerable spread in the data, it was felt that either mechanism could be used to explain the observed data within the precision of the data and assumptions made in devising the mechanism.

Spatial limitations preclude inclusion of these curves, which however may be found in (3). Work now under way and proposed for the future in this Laboratory may indicate which is the correct mechanism in the explanation of the drift in rate constant for any given batch run made.

Use of the first mechanism indicates an empirical equation for use after initial conditions

$$dp_{\mathrm{NO_2}}/dt = k(p_{\mathrm{NO_2}})^2 p_{\mathrm{ROH}}) + W(p_{\mathrm{HNO_3}})^{1.5} + (p_{\mathrm{NO_2}}/p_{\mathrm{oNO_2}})^2(p_{\mathrm{ROH}}/p_{\mathrm{oROH}})$$

where the partial pressures are given in mm. and the indicated rate is the forward reaction rate only. Indicated values of k and W are given in Table III.

TABLE III

W, k AND W/k FOR DIVERS ALCOHOLS 25°, $S/V = 0.3$ CM.$^{-1}$

Alcohol	W	k	W/k
Methanol	0.07	0.029	2.4
Ethanol	.13	.034	3.8
n-Propanol	.22	.057	3.9
Isopropyl	.10	.031	3.2
t-Butyl	.028	.015	1.9

Effect of Nitrites, Oxygen, Water.—These components were added in the initial feed, mixed with the alcohol used and at various partial pressures.

Nitrites and oxygen showed no effect on the partial pressure–time data for forward reaction.

Water was found to have a slight catalytic effect. The effect was undetectable at 0.1 and 0.2 mm. partial pressure. Rates increased by about 30% when 2 mm. water vapor was present. This effect was not nearly enough to account for the progressive drift of "k" values previously noted and discussed.

The very first run made with added water vapor showed anomalously high rates of NO_2 disappearance which could not be duplicated later. Not only was rate of reaction changed, but the reaction went far beyond the previously observed equilibrium composition. The significance of this observation (or lack of it) has not been ascertained.

Effect of Surface.—Results presented in the earlier sections of this paper were taken in a reactor having an approximate surface to volume ratio of 0.3 cm.$^{-1}$. Other data taken in a smaller diameter reactor with S/V approximating 1.0 cm.$^{-1}$ indicated an identical initial rate law to hold, but the rate constants obtained were approximately twice those obtained in the larger apparatus. Data taken when the reaction was run in the presence of glass wool (S/V approximately 1000) indicated reaction rates five to ten times those without the

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(3) A. M. Fairlie, Jr., Thesis, University of Notre Dame, 1952.

wool for comparable partial pressures. Thus surface of the Pyrex apparatus used has a definite influence on the reaction. However, it does not appear that initial rates are directly proportional to S/V ratio as would be the case if the reaction were completely surface catalyzed. At present work on the effect of surface is being done in this laboratory.

Effect of Temperature.—Data was taken for methanol only as described previously, at 0, 15 and at 25°. The method used at the lower temperatures had the limitation that data could not be taken earlier than four seconds after the outset of reaction, and the technique used was not identical to that at 25°. Thus it is felt that the data presented should be used only as an indication of the general trend of the variation of reaction rate with temperature.

Table IV indicates typical results obtained.

TABLE IV

3.0 mm. NO_2, 3.0 mm. methanol charged, $S/V = 1.\ \text{cm.}^{-1}$

Time, sec.	25°	15°	0°
	NO_2 reacted	NO_2 reacted	NO_2 reacted
20	0.50 mm.	...	...
6	...	...	1.5
4	...	0.6	...
	Rate = 1.5 mm./min.	Rate = 9.0 mm./min.	Rate = 15 mm./min.

It will be noted that reaction rate increases with decreasing temperature, indicating a "negative temperature coefficient." The magnitude of the rate change indicates an "activational energy" of −16,000 ± 3000 cal./g. mole.

Discussion of Results.—The reaction process itself is not as expected from the powerfully oxidizing nature of nitrogen dioxide. Oxidation is not appreciable, but rather an internal oxidation–reduction occurs within the two nitrogen atoms entering the reaction. Two quadrivalent nitrogens produce one trivalent and one pentavalent nitrogen. Alcohols thus react similarly to water, the difference lying principally in the stability of the nitrite formed.

The improbablity of termolecular collisions and the anomalous temperature effects strongly suggest that the rate determining step is a bimolecular reaction of N_2O_4 (in equilibrium with NO_2) with alcohol (or with alcohol associated with catalytic agent). Expressing all partial pressures in mm., $p_{N_2O_4} = (2.1\ 10^{-13}\ 10^{+14,500/4.57T})p_{NO_2},^2$ and rate of reaction will then be given by

$$\mathrm{d}p_{NO_2}/\mathrm{d}t = (k_r)(2.1\ 10^{-13}\ 10^{+14,500/4.57T}\ (p_{\mathrm{alc}})p_{NO_2})^2$$

It is felt that the error in the value of −16,000 cal./g. mole experimentally found is of such a magnitude that the k_r above may have a normal temperature dependance. However, activational energy for the reaction of N_2O_4 with alcohol can be at most only a few thousand calories.

Such a mechanism satisfactorily explains the experimental results but it does not preclude a mechanism of the type

$$NO_2 + ROH = NO_2{\cdot}ROH$$
$$NO_2{\cdot}ROH + NO_2 = HNO_3 + RONO$$

which in the end would give an over-all rate equation of the same form as that obtaining when N_2O_4 is assumed as an intermediate. Further experimental results at higher pressures will have to be obtained in order to establish unequivocably the true course of reaction. Such work will be made experimentally difficult by the high reaction rates encountered.

Since the rate controlling step has a low activation energy, in all probability the role of the catalytic agent accelerating the reaction in the later stages lies in increasing the frequency factor of the rate constant.

The relative values of the reaction rate constants for both simple and catalytic processes show the common trends found in organic chemistry, namely: decreasing reactivity in the sequence, primary secondary, tertiary and increasing reactivity as carbon chain lengthens. It is interesting to note that the alpha hydrogen seems to have little effect on the reaction as evidenced by the considerable reaction rate constant exhibited by the reaction of NO_2 with *t*-butyl alcohol.

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