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ANNUAL REPORT

ONR 392 (00)

Effect of Temperature, Surface and Divers Reagents on the Kinetics of the Vapor Phase Reaction, $2NO_2 + ROH \rightleftarrows HNO_3 + RONO$ at Low Pressure.

J. C. Treacy
Director

University of Notre Dame
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INTRODUCTION

While the reaction between Nitrogen dioxide and alcohols was noted as a "decolorization of the NO_2" by Harris and Siegel (1), the stoichiometry of the reaction and the reaction products were not identified until recently when this was done chemically by Treacy (2) and spectroscopically by Yoffe and Gray (3). These investigations seem to indicate the stoichiometry to be:

$$2NO_2 + ROH \quad RONO + HNO_3$$

where RONO denotes the nitrite ester of the alcohol used.

Carberry (2) initiated the investigation of the kinetics of the forward reaction (as written above), and found that the initial rates were second order with respect to NO_2 and first order with respect to Methanol. This reaction was run in a cylindrical tube 4.5 cm in diameter. Initial reaction rate constant was found to be 0.08 mm^{-2}/min, and a negative temperature coefficient was found to obtain. Since this was the pioneer work in the field, the best techniques and equipment were not discovered until very near the end of the work and hence there was considered to be a considerable lack of precision in the work finally reported.

Fairlie (2), working under Office of Naval Research Support, in this laboratory, undertook to re-evaluate the work of Carberry and to extend it to four other of the lower alcohols. The work was at 25°C only and was done in a large cylindrical reactor of diameter 14.5cm to eliminate surface effects if possible. The data taken substantiated the work of Carberry inasmuch as it indicated initial reaction rate equations for methanol, ethanol, n-propanol, i-propanol, and t-butanol to be second order in partial pressure of NO_2 and first order in alcohol. Fairlie found in addition that the reaction was evidently autocatalytic, for rate constants computed from the initial rate law were found to increase with extent of reaction and with time elapsed from the outset of reaction. Equilibrium constants were established with substantiated the stoichiometry previously indicated. Initial rate constants varied from 0.03 to 0.05 $^{-2}$ $^{-1}$

Meloche (3), (also under ONR sponsorship) investigated the kinetics of the reverse reaction using the same apparatus used by Carberry. HNO_3 was mixed with Methyl Nitrite and the rate of appearance of NO_2 was noted. Considerable experimental difficulty was encountered in measuring initial amounts of HNO_3 used and the final indirect method was left a considerable margin of error in the results. Nevertheless, the equilibrium values attained checked those of Fairlie, and an intial mechanism that was first order in both Nitrite and Nitric acid could be deduced. Results also tied into those of Fairlie inasmuch as rate constants for the reverse reaction were found to decrease with extent of reaction as might be predicted from the behavior of the forward "constants".

Based on these results, a mechanism was postulated that involved a gas phase reaction between N_2O_4 (in equilibrium with 2 NO_2) and alcohol, with the autocatalytic effects being cuased by traces of a decomposition product of HNO_3 (such a N_2O_5, or NO, or N_2O_3). The fact that Fairlie obtained a rate constant for the initial stages of the methanol reaction whose value of 0.03 was much less than the 0.08 of Carberry was laid to the inexactitude of the Carberry results.

Thus at the outset of the current year of ONR sponsored work, only the most meager indication as to temperature effects on the reaction was known, and practically nothing was known as to the effect of other oxides of Nitrogen on the reaction, or their possible relation to the autocatalytic effect noted. Since cheap commercial sources of NO_2 would in all probability contain large amounts of NO, it was of considerable interest to note the effect of this variable. Also, it was thought to be of considerable interest to test the often postulated role of N_2O_3 in the formation of nitrites when mixtures of "Nitrous gases" are used in reaction with organic materials, a postulation often found in the literature of organic chemistry.

EXPERIMENTAL

TEMPERATURE EFFECTS

In order to determine the effect of temperature on NO_2alcohol reactions a special cylindrical reaction cell was obtained. This had pyrex windows sealed on the ends and was jacketed for circulation of heated (or cooled) water. The largest cell available commercially had an internal diameter of 2.5 cm and a volume of 147 cc.

This cell was precisely calibrated as to volume and was connected thru ground glass fittings and stopcocks to two calibrated bulbs fitted with manometers for determination of initial amounts of alcohol and NO_2 used.

The light absorbtion caused by the NO_2 (the only colored material present in the reaction) was used to follow the course of the reaction. Light from and unfrosted incandescent bulb was filtered to remove light photochemically active on NO_2, focused to a parrallel beam, collimated and passed into the reaction cell. In order to achieve better precision the length of light path was doubled by reflecting light from the far end of the cell from a plane mirror back through the reaction mixture and thence from a small inclined plane mirror placed in the initial light path to a photronic photocell. Aside from the focusing effect, this doubling of light path was achieved in much the same manner as the light beam is removed from a reflecting telescope. The output of the photocell was used directly to activate a galvanometer (Gen El Cat 32C245). Thru use of shutters, light could be made to impinge on the cell directly from the source, thus providing a method of standardizing and checking initial intensity, which was done with some frequency during each run made.

Light intensity was adjusted manually to full scale galvanometer deflection at the outset of each run. An empirical calibration curve was determined relating partial pressure of NO_2 to galvanometer deflection. After it had been determined that other reactants and products had no effect of this deflection, the calibration curve could be used directly to translate readings to partial pressure of NO_2 present at any time during a given run.

A large insulated reservoir was used as a source of water which was heated electrically or cooled with ice to the desired temperature of the run. This water was circulated with a small centrifugal pump thru the water jacket of the reaction cell, in order to provide the desired isothermal conditions for reaction. Temperature variation throughout a run was at most 1°C.

After the desired temperature condition had been set and circulation established, the system was evacuated to 0.1 mmHg (McLeod gauge). The desired partial pressures of NO_2 and alcohol were then admitted to the separate measurement bulbs from a source of cp liquid alcohol from which all air had been pumped, and from a lecture bottle of NO_2 supplied Matheson Co., Joliet Ill. Partial pressures were read from a mercury manometer and were computed from the desired values that were to finally obtain in the reaction cell, the volumes involved and the temperatures Hg was found to react with NO_2 over a period of several weeks of use but to not effect results at all in the time taken to determine partial pressure to be used for one run. At the even minute indicated by a stopwatch, stopcocks leading from measurement bulbs to reaction system were simultaneously opened and gases flowed almost instantaneously into the reaction cell which was of much larger volume than the measurements bulbs. Galvanometer readings were then taken at appropriate time intervals, translated into partial pressures of NO_2, plotted (as pp NO_2 vs time) and the rate of reaction taken by differtiation of the curve obtained. Data was taken at various initial partial pressures of reactants and at divers temperatures, inorder that order at various temperatures, and temperature coefficient could be evaluated. Reactions were allowed to proceed until no detectable change in galvanometer reading could be detected in 20 minutes. This was taken as the equilibrium conditions and values of the "K" were computed using the stoichiometry previously noted.

EFFECT OF INITIAL THIRD COMPONENTS

The effect of Nitric oxide, etc on the reaction was evaluated in similar manner.. The apparatus used was the same as that of Fairlie as previously noted (see yearly ~~notebook~~ report, June, 1952 from ONR 392(00)), in which the reaction cell was cylindrical with diameter 14.5 cm and volume 18,700 cc $S/V = 0.3 cm^{-1}$. This apparatus was long enough so that one pass of the light thru it was sufficient to give the desired precision.

The desired reactants were measured and placed in the reaction cell as previously described, NO.(or other "third initial component") was mixed with one of the two key reactants with which it did not react, partial pressures of each being noted on an Hg manometer. Data were taken with partial pressures of NO_2 and alcohol constant with variable partial pressures of NO, HNO_3 etc to determine the effect of the third variable on initial rate. Later, data were taken in which partial pressure NO_2 and alcohol were varied in order to determine any effects on the overall order of the reaction.

Temperature was held at 25°C ± 1 by making the room into a "thermo-room".

RESULTS

The reaction was studied in a bath system at partial pressures up to ten mm Hg for all components used. Rate was followed photometrically, the NO_2 concentration being determined as a function of time.

It was found that:

(1) Addition of Nitric oxide did NOT affect initial rate. NO entered the reaction only in the later stages thru reaction with HNO_3, produced by the primary reaction. This secondary reaction was relatively slow compared to the primary reaction. Initial rate constants reproduced values given by Fairlie.

(2) Addition of divers Nitrite esters did not affect initial rate.

(3) Nitric acid addition in feed charge increased initial rate by 50%. And while the mode of addition of Nitric acid (either with alcohol or with NO_2), did not materially affect initial rate, it did affect equilibrium values observed, thereby suggesting that nitric acid reacts with ethanol alone but is inhibited from doing so when produced from the 2NO + ROH reaction.

(4) Acetaldehyde had no effect on initial rate. Thus traces of this material are not effective as an autocatalytic agent.

(5) The "negative temperature coefficient" previously reported by this laboratory was substantiated.

(6) Work on temperature effects was carried on in an apparatus having a smaller volume to surface ratio than that used previously (see 1952 annual report from this project). With the present apparatus, it was found that reaction rate depended on the second power of NO_2 partial pressure, but on LESS than the first power of the alcohol partial pressure. Furthermore, the "order with respect to alcohol changed with temperature used, from 0.3 to 0.8 as T varied from 0 to 75 degrees C. Since first order rate dependance on alcohol was found in the larger apparatus (ONR annual report, 1952), and only S/V ratio was changed, the effects was interpreted to signify that a surface reaction of an order less than unity is present and thus becomes relatively more important at high values of S/V.

(7) Reaction rates at comparable pressures were observed to be greater with higher S/V ratio. Because of the change in overall rate law no simple values of reaction rate constant could be computed. However, values of (k[illegible]) are computed for the two simultaneous rates in the mechanism as postulated.

(8) Different rate effects were noted when alcohol or NO_2 was admitted first to the reaction cell, tending to substantiate the conclusion that surface effects are of some importance at higher S/V ratios.

(9) Equilibrium value at 25° were substantially as noted in the larger apparatus in previous work, thus indicating that the effects noted were not simply caused by simple removal of appreciable amounts of reaction material for the gas phase by simple absorbtion. Likewise these results indicate that no basic undetected measurement errors were made.

(10) Heat of reaction value computed from equilibrium constants of ethanol was in reasonable agreement with (6Kcal) values computed from standard heats of formation and combustion. H = -14,000 cal/gmol. Thus ΔS^{o} was $^{-25}$cal/°mole for the reaction $2NO_2 + C_2H_5OH = C_2H_5ONO + HNO_3$ and the standard molal entropy of ethyl Nitrite was + 84. (Stand, State, 25°, 1 Atm).

Quantitative Results are Presented Graphically in the following pages.

Discussion (temperature and surface effects)

Figure 1 indicates quantitatively the change in "order" with respect to alcohol that was noted at the divers temperatures investigated and with surface to volume ratio equal to 1.4 cm^{-1}. At all temperatures, it was found that the reaction rate varied at the second power of the NO_2 partial pressure (first power of N_2O_4). It was thus thought to be expedient to express the data with the NO_2 dependance already "corrected".

It was found that this data could be also expressed without significant error in the form....$dp_{NO_2}/NO_2^{2}\,dt = k_1\,(alc) + k_2$, if the constants k_1 and k_2 were chosen of the correct order of magnitude. These values as computed are tabulated in Table 1.

Table 1	Temperature °C	k_1 (L^2/moles^{2}sec)	k_2(L/mole sec)
	0	6.0x10^5	145
	25	3.6	53
	50	1.8	6.7
	75	0.3	1.6

It is to be noted that values of k_1 decrease with increasing temperature, "activational energy" being 8.5 Kcal/gmol. Values of k_2 fall off rapidly with increasing temperature. A plot of $\ln k_2$ vs $1/T$ (figure 2) indicates that activational energy for this constant is of the order of -[illegible] kcal/gmol. Both constants exhibit a negative temperature coefficient as noted by previous workers(2).

Values at 25°C seem to be somewhat high compared with the other value listed. If allowance be made for this, it is to be noted that the value of k at 25°C for ethanol shows very good agreement with the value of 2.0 10^5 as reported by Fairlie (2) whose work was done in an apparatus with surface to volume ratio = 0.3 cm^{-1}.

It is then tentitively postulated that the reaction of NO_2 (or N_2O_4) with alcohols (data for t-butanol at 25° C show much the same effects as did the ethanol data) proceeds according to two simultaneous reactions. The first reaction is a vapor phase reaction and initially represents a simple second order reaction between N_2O_4 and the alcohol. The second reaction is surface catalyzed and is essentially zero order in alcohol. The surface reaction process is tentitively postulated to be an adsorbtion of ROH on the walls to make an adsorbed species hereafter denoted by "X". This species then reacts with N_2O_4 to form the products of the overall reaction. Thus:

$$ROH + S \underset{kb}{\overset{ka}{\rightleftharpoons}} X$$

$$S = S_o - X$$

$$N_2O_4 + X \xrightarrow{kc} NO_3 + RONO + S$$

Therefore; $$\frac{dx}{dt} = 0 = ka\,(ROH)(So-X) - k_b\,X - k_c\,(X)\,(N_2O_4)$$

$$X = \frac{ka\ (ROH)(SO)}{ka(ROH) + k_b + k_c\,(N_2O_4)}$$

which for k_b and k_c small with respect to ka reduces to:

$$X = So$$

and, expressing rate in on a moles per unit volume bases;

$$\frac{d\,NO_2}{dt} = k_c(So/V)(N_2O_4)$$

This is equivalent to assuming that equilibrium adsorption of is the controlling step of this reactioh.

Thus combining the homogenous and heterogeneous rates, overall rate is given by:

$$dNO_2/dt = N_2O_4\ (k_1 alc + k_a\ (S/V)$$

which is in agreement with the experimental data.

Data taken in this investigation where NO_2 and alcohol were added non-simultaneously to the reactor tend to substantiate this postulation. When NO_2 was added first, little effect was noted on the rate. However, when alcohol was added first, rate was observed to be almost double that observed for simultaneous addition of reactants. This is interpreted to mean that with the separate addition, time was allowed so that active centers requiring a higher activation energy for alcohol adsorption were given a chance to adsorb alcohol, thus actually adding to the catalytic activity of the walls. Since NO_2 does not show a rate effect, it is inferred that it has little effect on the reaction through means of adsorption.

A further observation lends credence to the supposition that alcohol adsorbs on pyrex walls. At zero degrees, pure alcohol was admitted to the reaction cell for purposes of noting light absorbtion effects if any. At higher temperatures, no effect was noted on galvonometer reading when alcohol was admitted, but at zero, a steady slow drift of the galvanometer output was noted, indicating that light was somehow being adsorbed, scattered or reflected. Since the pressures were considerably below the vapor pressure of alcohol, this is interpreted to mean that a film of adsorbed alcohol was being formed on the pyrex windows leading to reflection according to Fresnel's law. This effect throws some doubt on the validity of readings taken a zero degrees C, and for this reason equilibrium data taken at zero were discarded. Since the effect was only noticeable after several minutes had elapsed, initial rate data were included and are felt to be reasonably valid.

It is interesting to note that since the heterogeneous part of the rate equation is dependant on the S/V ratio, the catalytic rate would have been much less in evidence in the work of Fairlie (2). This work was done in an apparatus with S/V approximately 1/5 of that used in the present work. Making the appropriate correction for S/V, it may be determined that an apparent order of 0.9 would obtain in the Fairlie work (with respect to alcohol). Such a slight deviation from unity was masked in the experimental uncertainty of the points plotted for order determination. In fact certain of the Fairlie data did tend to indicate slopes less than unity but at the time this was attributed to experimental errors.

Equilibrium data taken with the higher S/V indicated an average equilibirum constant of 0.97atm^{-1} at 25°C which compares very favorably with the value of 0.85 reported by Fairlie et al. This indicates that there was no internal inconsistancies caused by experimental method errors that might preclude comparing the two sets of data. A plot of log K vs 1/T for ethanol was used to determine the heat of reaction. This value was -14.0 Kcal/mol for the reaction of $2NO_2$ with one alcohol.

This value enabled the computation of heat of combustion of Ethyl Nitrite within 6 Kcal of the value tabulated in "Handbook of Chemistry and Physics". Standard molal entropy of Ethyl Nitrite (25°C, 1 atm) was estimated to be 74 cal/°Kmole. This last value may be compared to a rough statistical calculation assuming free internal rotation about all applicable bonds which gave a value of 90. Thus it may be inferred that free internal rotation does not occur within the EtONO molecule.

an investigation of rate of reaction in the later stages of reaction substantiated the results of Fairlie in that reaction rates above those that would be predicted from the stoichimetry and the initial rate law obtained. Thus the products are seen to be autocatalytic to the reaction, and this effect is believed to be in addition to the surface effects already noted.

The temperature effects are by no means anomolous when the overall mechanism is considered. The rate law evaluated is based on NO_2 as a reactant. The improbability of termolecular collisions would indicate that in all probability the reactive species in N_2O_4 rather than 2 NO_2. Since N_2O_4 decreases in amount with increased temperature ($N_2O_4 = NO_2{}^2\, e^{\Delta S/R}e^{-14,500/RT}$), this effect counterbalances the increased value of specific rate constant at higher temperatures. Thus for K_1, the simple vapor phase reaction constant, activation energy is approximately 16 kcal. It is to be expected that adsorption on pyrex would produce such bonding as to reduce the activational energy of the reaction process. Thus the catalytic surface rate might be expected to have a smaller value of E as compared to the gas phase rate. This smaller value of E, combined with the 14,500 for the NO_2-N_2O_4 equilibrium accounts for the negative value of E indicated by the trend of the heterogeneous constants.

DISCUSSION

(Effect of products and divers third Components on initial reaction)

The increase in rate over what would be predicted from the initial law and the stoichiometry as observed by Fairlie in the later states of the NO_2-alcohol reaction suggested the desirability of locating the agent causing this autocatalysis.

With NO_2 there is always the possibility of oxidation reactions. Thus the roles of NO and of acetaldehyde were investigated. These were found to have no effect on initial values of the reaction rate as is indicated in table 2. (4.0 mm NO_2, 2.0 mm EtOH Charged)

mm NO	k_o (Rate/$NO_2{}^2$ROH) $mm^{-2} min^{-1}$
0.0	0.0275
1.0	0.029
2.0	0.029
6.0	0.0275
12.0	0.0275
mm CH_3CHO	
0.0	0.033
6.0	0.0335

With NO constant, NO_2 and alcohol partial pressures were varied to determine the possible effect of NO on order of the reaction. It was found that rate constants computed from these data were without significant drift as indicated . Values of "k" taken with NO_2 = 4mm, NO = 6mm, with Alcohol at 1.0,1.5,2.0 and 2.5 were respectively, .046, 1.033, 0.031, 0.036. This variation is within the errors involved in the Fairlie investigation, and it is felt that they do not indicate a variation due to NO, but rather exhibit the effect of surface as indicated in the previous sections of this report.

NO was observed to have an effect on the later stages of the reaction as expected from the reaction of HNO_3 product with NO. This secondary reaction ($2HNO_3 + NO = 3NO_2 + H_2O$) was evidently much slower than the primary reaction, for pressure-time data with and without NO were identical until as much as 40% of the initial NO had reacted. Under such conditions, the primary reaction had almost come to its equilibrium value before NO_2 began to reappear due to the secondary reaction. This last is in direct contradiction to the observations of the writer taken on the same apparatus in 1949. Then, as little as 1/2 mm of HNO_3 was observed to react practically instantaneously with one to two mm NO. Reaction rate was so rapid as to defy taking data with the apparatus. Thus it is inferred that the presence of the divers other species (Alcohol and Nitrite ester) has an inhibitory effect on the nitric acid-NO reaction. Since this was not part of the primary investigation, the subject was not pursued farther. It may well be that Nitrite inhibition of Nitric acid reactions in general may prove to be of considerable value in explosive and nitric acid oxidation reactions generally.

Since Veloche had found that the reverse reaction proceeded much more rapidly initially than after some reaction had taken place (after due account had been taken of the stoichiometry) it was considereed possible that the products of the forward reaction themselves might have catalytic effects. To evaluate this effect, ethyl Nitrite was added to the feed charge
Computed rate constants with 6mm EtONO and 0.0 mm ETONO were 0.025 and 0.028 respectively.

Due to the low vapor pressure of HNO_3 only small amounts of this material could be added in the feed charge. However an increase in rate was noted. Initial rate constant changed from 0.028 to 0.038 on addition of 0.5mm of HNO_3 vapor. While this is a significant change and is in line with the Fairlie postulation that HNO_3 decomposition products are the cause of the autocatalystic effect, the magnitude of the effect is too small to account for the results reported by Fairlie. The HNO_3 used was taken directly from stock fuming HNO_3 and presumably contained the maximum amounts of N_2O_5 etc.

Since the autocatalytic effect is NOT caused by products directly, or by products due to oxidation, or by divers Nitrogen oxides, there are only a very few possible species that could be postulated to cuase the rate changes noted. Of these, Alkyl Nitrates are felt to have the best possibility of causing the noted effects. Presumably these nitrates might be formed from the products of the NO_2-alcohol reaction....HNO_3 + RONO = HONO + RNO_3. It has not been felt to be desirous to evaluate this postulation experimentally due to the danger involved in use and storage of the lower parrafin nitrates.

The finding of this investigation that NO does not affect reaction rate for nitrite formation is of considerable interest in organic chemistry. It was expected that N_2O_3 formed from the divers nitrogen oxides would react directly and rapidly with the Alcohol to give a series of reaction steps:

$$NO + NO_2 = (eq)\ N_2O_3$$

$$N_2O_3 + Alc = RONO_2 + HNO_2$$

$$HNO_2 + Alc = RONO + H_2O$$

with a rate given by : $dNO_2/dt = k\,(NO_2)\,(NO)\,(Alc)$. If any such mechanism had been competing with the $2NO_2$ + ROH reaction in significant amounts, an increase in NO concentration would have increased the indicated reaction rate. Such was not observed, and hence it may be concluded that the only effect of NO is the removal of HNO_3 product. When this secondary reaction is considered with the primary reaction, and the equations are added, an overall stoichiometry exists that is indentical to that obtained from the N_2O_3 mechanism. Evidently N_2O_3 is formed in such small amounts that is has no noticeable effect on the N-oxide-alcohol reactions.

* * *

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(2) Fairlie, Carberry & Treacy, to be published, J.A.C.S. July, 1953.

(3) Yoffe & Gray, J.C.S. 1412 (1951)

(4) Meloche, Dissertation, University of Notre Dame (1952)

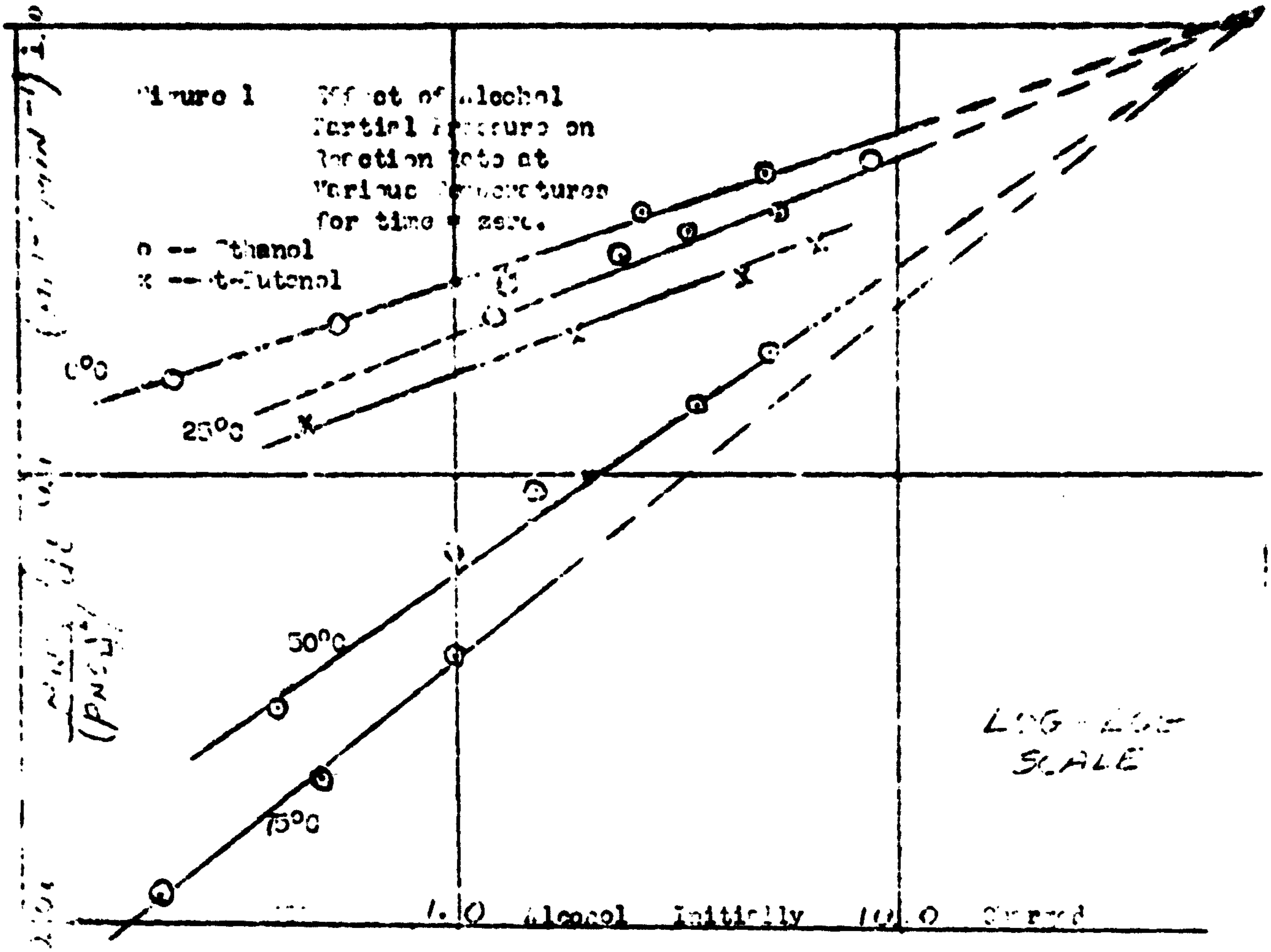

Figure 1 Effect of Alcohol Partial Pressure on Reaction Rate at Various Temperatures for time = zero.

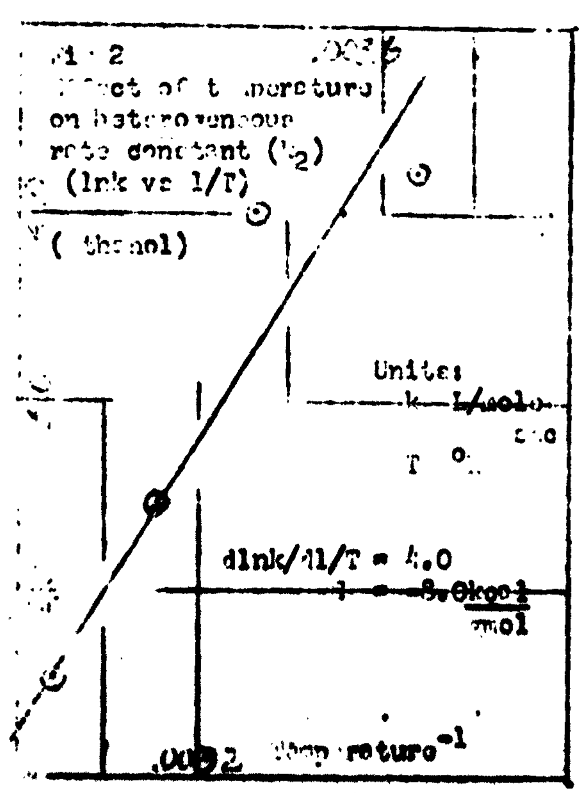

Fig. 2 Effect of temperature on heterogeneous rate constant (k_2) (lnk vs 1/T) (Ethanol)

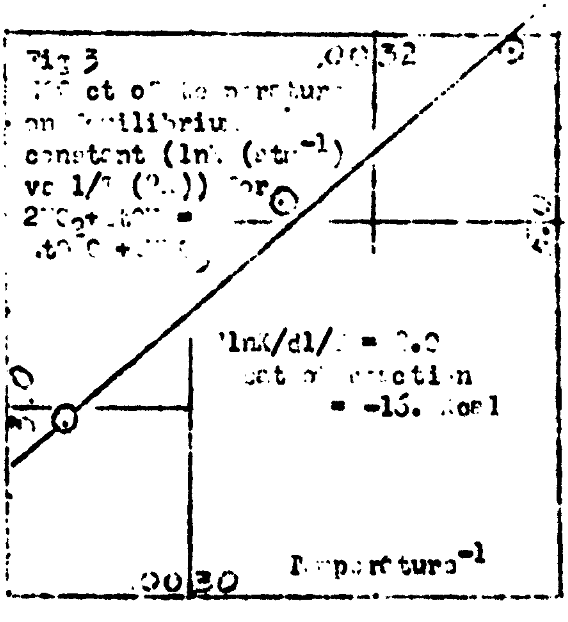

Fig 3 Effect of temperature on Equilibrium constant (lnK (atm^{-1}) vs 1/T (°K)) for [illegible]

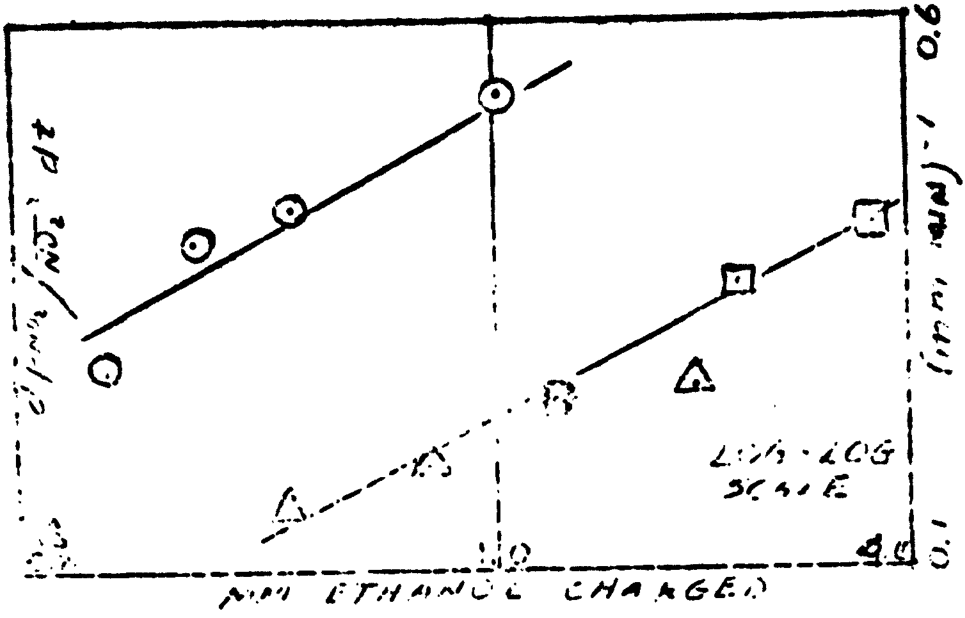

Fig 4 The effect of non-simultaneous addition of alcohol and O_2.

o... NO added [illegible]
....O_2 added [illegible]
...simultaneous addition

25°C.

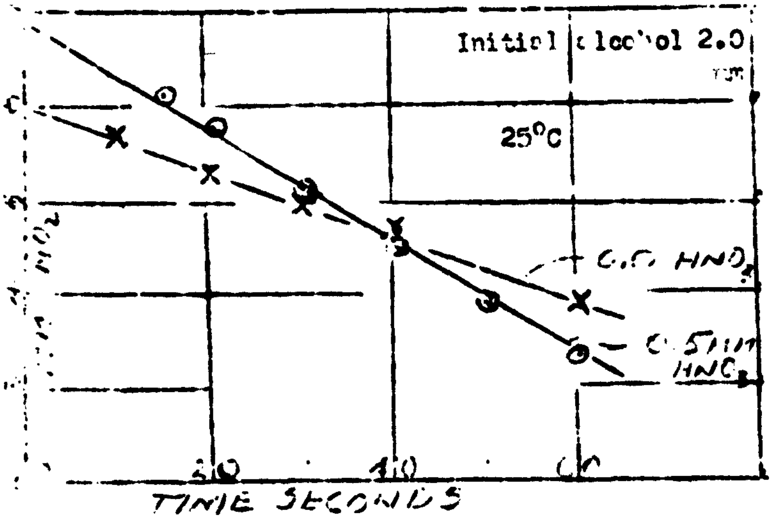

Fig 5 Effect of addition of 0.5 mm of HNO_3 vapor in initial charge.

Initial rate constants:
0.029 without HNO_3
0.032 with HNO_3

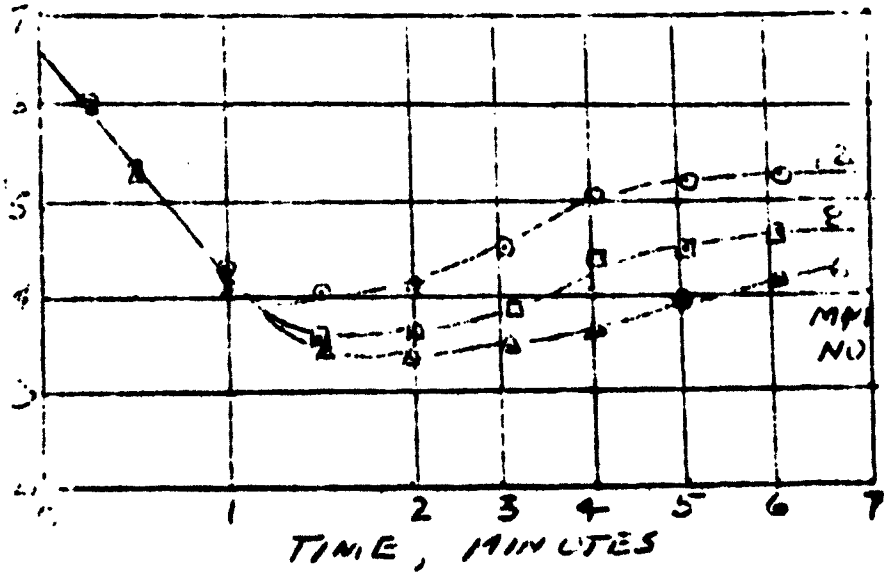

Fig 6 Effect of NO addition as indicated to an initial charge of 5.0 [illegible] O_2, 2.0 [illegible]

Similar curves were obtained at other pressures of O_2 and alcohol.

25°C.

(note change in axis scale)