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A STUDY OF THE RATE OF REACTION OF NO_2 WITH VARIOUS ALCOHOLS AT LOW TEMPERATURES AND PRESSURES

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The present work extends the work of Fairlie Carberry and Treacy and is concerned with reaction rates for the reaction, $2NO_2+ROH \rightarrow HNO_3+HONO$ (1). Surface effects and temperature coefficient were evaluated for reactions involving the C_1 to C_4 aliphatic straight and branched chain alcohols. The reaction has been found to be surface controlled with alcohol being the adsorbed species and N_2O_4 reacting directly form the vapor phase. Practically no reaction was observed with paraffins wax surfaces, while rates of considerable magnitude were observed when glass, aluminum, and teflon surfaces were used. Reaction rates as well as equilibrium conversions were considerably reduced as temperature was increased. A rate law is postulated and experimental values of constants invived are tabulated.

The work of Fairlie, Carberry and Treacy (1) indicated that the reaction rate of NO_2 with ROH was third order as indicated by the stoichiometry, and meager indications of surface effects and a negative temperature coefficient were reported.

The present work was undertaken in order that temperature and surface effects might be quantitatively evaluated, enabling a more complete understanding of mechanism and eventual use of this reaction in the production of nitrite esters. This paper describes the method used in studying this rapid surface reaction, presents experimental results, postulates a mechanism and rate law and gives values of rate and equilibrium constants for use with this rate law.

EXPERIMENTAL

The photometric method was used for following the course of the reaction. Of the species present, only NO_2 was found the absorb the filtered green light used (4500-5000A). With this light, filtered to remove wave lengths photochemically decomposing to NO_2, NO_2 was detectible to well below 0.1mmHg and could be determined to ± 0.03mm throughout the range of partial pressures used.

Apparatus: The reaction was run in cylindrical cells of length 122cm with diameters varying so as to give surface to volume ratios of from 0.9 to 1.4 cm^{-1}. With one exception these cells were immersed in a circulating water thermostic bath capable of controlling temperature to ± 0.1°C. The ends of the cells protruded from the bath and were closed with plane glass windows for ad-

(1) A.M. Fairlie Jr., J.J. Carberry, and J.C. Treacy, JACS, 75 3786(1953)

mission of the measurement light beam.

Light was obtained from an incandescent source, filtered, collimated and focused, and reflected through the reaction cell by means of plane mirrors. Provision was made to pass a portion of this beam through a blank tube, enabling a rapid check of the constancy of the source. Light leaving the reaction cell was reflected with mirrors upon a photronic photocell which actuated a sensitive galvanometer whose output was recorded. Galvanometer output was converted to values of partial pressure of NO_2 by means of an emperically determined calibration curve.

Initial amounts of reactant were determined by admitting these from storage into evacuated bulbs which were precisely calibrated as to volume. Partial pressures were determined manometrically at the temperature to be used in the following run. With the volume of the reaction cell being also known, this enabled computation of initial partial pressure that obtained for each reactant when reactants were flashed into the reaction cell. In these computations, due account was taken of residual amounts left in measurement bulbs and of the NO_2-N_2O_4 equilibrium.

Data involving pyrex glass were taken directly within the cells used. With surfaces of paraffine, teflon and Aluminum, tubes (or coated glass tubes) of one foot length were inserted end to end with small clearances into a much larger containing cell. The light beam was passed through the inside of these tube sections. The reaction cell thus consisted of the volume within the inserted tubes, which was in free comunication with the much larger outside volume. In this work only data at 25°C were taken and temperature control was obtained by adjusting room temperature to 25° ± 0.5.

Stopcocks lubricated with silicone grease were used after it was determined that these were unreactive in the presence of NO_2.

Procedure: Thermostats were brought to the desired temperature, and the entire system was evacuated to 0.05mm. No attempt was made to flame apparatus or to reduce pressure with Hg diffusion pump. The desired pressures of alcohol and NO_2 were admitted to the measurement bulbs and determined manometrically. Alcohols were boiled before each run to eliminate dissolved air etc and were used directly from CP sources as careful purification had previously been shown not to affect reactions or reaction rates within the limits of precision obtainable. NO_2 was taken directly from lecture bottles supplied by Matheson Co. and contained less than 0.5% N_2, O_2 etc.

The light intensity was adjusted to a desired reading and the reading of the "blank tube" was recorded. This reading was checked with frequency during each run. Occasional variance of this blank reading caused little difficulty, but in such cases the data was completely discarded and rerun.

On the even minute of a running stopwatch, stopcocks admitting reactants to the reaction cell were rapidly and simultaneously opened. Galvanometer readings were then taken at appropriate intervals. Entrance errors due to non-simultaneous stopcock opening etc were found to be undetectable inasmuch as computed NO_2 readings and actual photometric determination checked very well.

Galvanometer readings were converted to partial pressures of NO_2 by means of an empirical calibration curve. Partial pressure NO_2 was then plotted versus time on Cartesian coordinate paper and rates were determined by graphical differentiation.

Initial values of the reaction rate were divided by partial pressure NO_2 squared and by partial pressure alcohol to give an indicated rate constant "k" whose reciprocal is shown as a function of alcohol partial pressure in a subsequent section of this paper. From these plots, values of the various constants may be deduced as well as a rate law.

Runs were alowed to proceed until no galvanometer changes could be detected over a period of 20 minutes. This was assumed to represent equilibrium and values of equilibrium constant werecomputed from such data, with the $2NO_2+ROH=RONO+HNO_3$ steichiometry being assumed.

Serious limitations on the use of this method preclude use ouside the ranges of partial pressures used in this work. Partial pressures are limited by the vapor pressures of the alcohols and by formation of liquid phases in the presence of HNO_3 at partial pressures much less than the vapor pressures of acid and alcohol At higher temperatures where these limitations no longer apply, reaction rate becomes so slow, and equilibrium conversion so low that precision in the measurements are poor.

RESULTS

Using this apparatus and procedure, rate and equilibrium data were taken for all lower alcohols, C_1 to C_4 except isobutanol at 25°, 40° and 55°C, in pyrex apparatus with $S/V = 0.9\ cm^{-1}$. Data were taken in pyrex apparatus for ethanol only at $S/V = 1.4$, and for methanol, ethanol, and n-propanol on paraffine teflon and Aluminum surfaces at $S/V = 1.0 \pm 0.1$.

The vapor phase rate was found to be negligible with respect to wall reaction rates. Reaction rate was found to be exactly proportional to the second power of the NO_2 partial pressure. A rate law of the form

$$-dNO_2/dt = k_s K_A K_1 (S/V)(1/(1 + K_A A))(NO_2^2 A)$$

was found to hold for all alcohols investigated, for initial conditions. K_1 denotes the equilibrium constant for the $2NO_2 = N_2O_4$ equilibrium, K_A denotes an adsorbtion equilibrium constant, and k_s a surface rate constant.

Denoting the group $k_s K_A K_1 S/V$ by "a", it was found that "a" has an apparent activational energy of -17 to -20 Kcal. Heats of adsorbtion affecting K_A were determined to be of the order of -7 to -12 Kcal.

Complete data are found in Dissertations filed with the library, University of Notre Dame.

Paraffine Surface:

These data were taken by passing a light beam through sections of coated

glass tubing placed within the same cell in which the data of Fairlie (1) were taken. In the previous work the light beam had been passed through the center of the cell and at a distance of 5-7 cm from any wall. The present "Paraffined cell" was placed at the bottom of the outer pyrex cell at such a position that specific rates close to 50% greater than those reported in (1) were obtained, without the use of an inner cell.

Rate data taken with the paraffine cell was found to be first order in alcohol, but with a specific rate constant less than half that reported in (1). Experimental values must be further corrected for the free communication of the paraffined cell with the larger exterior vacuum tight pyrex container. If no reaction had taken place within the paraffine surface, an indicated ficticious rate would appear to take place due to withdrawal of NO_2 as reaction takes place in the outer tube with a three yeilds two etoichiometry. With R = experimental rate within the wax cell, R_o the rate outside this cell, X the mole fraction NO_2 and R_g the true reaction rate within the wax cell,

$$R_g = (R - (X/2)R_o)(1/(1-X/2))$$

Data taken are Tabulated in Table 1, k_o values being corrected for free communication using values of specific rate constant 50% greater than those given in (1) as indicated by present work, at the location used for paraffine cell.

TABLE 1 Rate Data in Paraffine cell (S/V =1.0, 25°C)

Alcohol	NO_2 mm	ROH mm	Rate mm/min	"k"	k_o
Methyl	3.48	2.89	0.43	0.012	0.000± 0.003
	3.78	4.40	0.75	0.012	0.002
	3.33	6.60	0.88	0.012	0.005
					Av 0.002
Ethyl	3.58	1.41	0.31	0.017	0.001
	3.69	2.10	0.52	0.018	0.005
	3.64	2.72	0.56	0.016	0.005
	3.38	3.38	0.73	0.016	0.005
	3.08	4.46	0.70	0.017	0.009
					Av 0.005
n-Propyl	3.30	0.30	0.14	0.043	0.007
	3.13	0.86	0.37	0.044	0.019
	3.25	1.21	0.52	0.040	0.013
	2.73	1.56	0.48	0.041	0.020
					Av 0.015

Values of k_o as tabulatedindicate maximum values of vaporphase rate that could obtain. It is possible that at least part of these rates may represent heterogeneous reaction on the wax surface, a possibility that is likely in the light of the increasing rate obtained as the organic radical is made larger. Vapor phase reactions are at best slow compared with wall reactions and can be neglected with repect to heterogeneous rates obtaining with other sufaces investigated.

Pyrex Surface: Data were taken for all C_1 to C_4 Alcohols (except t-Butanol) at 25, 40 and 55°C with surface to volume ratio 0.9 cm^{-1}, and with ethanol only at S/V = 1.4

As the reaction was wall catalyzed, it was expected that rate equations of the form

$$-dNO_2/dt = (k_s K_A K_x S/V)(NO_2^2 A - HNO_3\ HONO/K_{eq})(\ 1/(1+K_A A + K_B NO_2 + \ldots))^n$$

would obtain. It has been found by four investigators working at various temperatures, pressures and S/V ratios that the reaction rate depends on exactly the second power of the NO_2 partial pressure. Thus K_B must be small. Under initial conditions, terms involving product are not involved in the rate law. Thus defining $k_s K_A K_x S/V = a$, and $-dNO_2/dt/NO_2^2\ A = k$,

$$1/k = (1/a)(1 + K_A A)^n$$

Figures 1 through 7 present the experimental data taken, 1/k being plotted against alcohol partial pressure with n=1 . Inasmuch as these plots resulted in straight lines, the assumption of n=1 is correct. Intercepts of these plots provide values of the composite constant "a" and combination of slope and intercept gives values of K_A.

The factor "J" appearing in the ordinate of Figures 1 to 7 represents (298-T)1000 / 298 RT and essentially corrects intercepts at higher T to those at 25°C enabling all data for one alcohol to be shown together for comparison purposes. Numbers appearing in ordinates of Fig 1-7 are apparent activational energies associated with the constant "a", in Kcal/gmol.

This method of presenting data is one that emphasizes any scatter in the data. Deviations from the curves drawn can be attributed to errors in graphical differentiation, for as little as 5% error in this operation will cause deviations of the order indicated in the plots.

Slopes of the plots were used to estimate values of the adsorbtion constant K_A at the three temperatures investigated. K_A was plotted vs 1/T and heat of adsorbtion estimated. Secondary and tertiary alcohols at 55°C gave slopes so near to zero as to be useless in the estimation of K_A. Heats of adsorbtion for these alcohols are based on values at 25° and 40°C only and are hence of less reliability.

Values of the constants at 25°C and values of energies of activation and heat of adsorbtion are given in Table 2. k_s, the true surface rate constant and its corresponding activational energy, E_s were computed with the assumption the N_2O_4 rather than 2 NO_2 is the true reactive species. Thus $k_s = a/K_A K_1 (S/V)$, and $E_s = E_a + 14.6 - H_A + 1.2$. 14.6 Kcal represents the heat of the reaction $2NO_2 = N_2O_4$, and the factor 1.2 compensates for changes in concentration with increased temperature, it having been determined that the factor $(T/298)^2$ closely approximates $\exp -1{,}200\ (298-T)/298RT$ in the short range used.

TABLE 2 Constants at 25°C, heats of Adsorbtion and Activation

Pyrex Surface

Alcohol	a_{25} mm^{-2}/min	K_{A25} mm^{-1}	k_{S25} cm/min	E_a	H_A Kcal/gmol	H_s
Methyl	0.33	0.83	48	-17.2	-8.3	+7
Ethyl	0.29	0.64	54	-18.7	-5.2	+2
n-Propyl	0.33	0.74	53	-16.2	-7.2	+7
n-Butyl	0.54	2.0	33	-15.0	-6.4	+7
i-Propyl	0.11	0.20	66	-19.0	-12.5	+9
sec-Butyl	0.25	0.60	50	-23.	-9.3	+2
t-Butyl	0.067	0.20	40	-16.	-10.	+8

At the outset of this work when reactor surface was new and clean, abnormally high rates were observed. Data was not reproduceable until four to five runs had been made. Thus clean glass surface is more highly catalytic than "used glass". After these intial runs, reproduceable data could be taken at any time indicating no further surface fouling.

In many runs an induction period was observed, expecially with the higher alcohols. Presence or absence of induction was evidently influenced by the length of time spent in evacuation of the reaction cell, but did not appear to influence rates obtained after the reaction began. Rates taken with or without induction fell on the same curve and were used interchangeably in plotting Figs 1-7. Rather than invalidating the data it is felt that these induction periods serve only to indicate that time required to come to adsorbtion equilibrium was of such magnitude as to be ineffective in varying results obtained. It is tentitively postulated that induction times observed represent times required by the system in the building up a first monolayer if this had been essentially stripped off by extensive pumping.

Data taken with ethanol in small reactors where intial mixing errors could be minimized using a non-simultaneous additions technique showed rate data comparable to that taken with simultaneous addition when NO_2 was added first, but considerably higher rates when the alcohol was added first. Thus it is indicated in a somewhat different manner that alcohol is the adsorbed species and not NO_2.

S/V Ratio: The effect of S/V could not be tested over long ranges. Figure 8 indicates that the constant a varied exactly in proportion of the S/V ratios involved (1.4/0.9). Thus rate is indicated to be proportional to S/V ratios in small reactors.

Teflon and Aluminum Surfaces: Data were taken using "free communication" technique similar to that used with paraffin surface. Rates are corrected for free communication, and were taken at 25°C for Ethanol and n-Propanol.

Corrosion data taken in this laboratory in the liquid phase indicates that aluminum and stainless steel stand up well to the peculiar condions of this reaction (no corrosion on stainless steel and 100 mg/sqdm/day under the worst conditions, for Al, less under other conditions). Thus these data were taken so that rates might be estimated within surfaces which might be of particular use under industrial conditions, as well as to evaluate the effects of inert organic surface and inorganic oxide (Al_2O_3) surfaces on the kinetics of this reaction.

Table 3 indicates that both adsorbtion K and surface rate k are reduced when teflon is substituted for pyrex surface, but not so much as to make this surface useless as a catalytic surface. Al (Al_2O_3) surface indicates a lesser surface rate constant, but greater adsorbtion K as compared to pyrex. Rates are not seriously reduced at these pressures.

TABLE 3 Rate and Adsorbtion Constants for Various Surfaces, 25°C
S/V = 1.0 ± 0.1 cm^{-1}

Material	Ethanol			n-Propanol		
	a_{25}	K_{A25}	k_{s25}	a_{25}	K_{A25}	k_{s25}
Pyrex	0.29	0.64	54	0.53	0.74	53
Teflon	0.12	0.35	34	0.67	1.41	51
Aluminum	0.22	0.80	29			

Rates after initial conditions: Fairlie et al (1) reported that the reaction was autocatalytic. The present work substantiates this. Rates taken after inital conditions are higher than predicted from the intial rate law. However whereas it was previously reported that this effect was dependant on the time elapsed from intial conditions to the time of measurement, this effect has not been found to apply in the present work. It has been found that rates after intial conditions are higher than predicted from the intial rate law and the postulated stoichiometry by a factor of $(1 + 0.8(NO_{2_0} - NO_2))$. Only typical data taken from runs using n-Propanol is shown in table 4. Very similar behavior was noted with other alcohols.

Table 4 Rate Data After Initial Conditions..n-Propanol, Pyrex Vessel, S/V=0.9
(values taken at random from runs at various initial pressures)

mm NO_2 reacted	Actual Rate/Rate predicted from intial law. 25°C	55°C
0.4	1.36, 1.4, 1.48, 1.48	1.2, 1.25, 1.35, 1.5, 1.35
0.8	1.6, 1.7, 1.75, 1.75	1.52, 1.53, 1.8
1.2	1.85, 2.0	1.87
1.6	2.2	

Equilibrium and Stoichiometry: Equilibrium was found to be a considerable limitation on extents of reaction. It was found that only with the grouping of terms as indicated by the stoichiometry $2NO_2+ROH=HNO_3+RONO$ could a constant value of the equilibrium constant be computed from the data taken with five fold variance in partial pressures of species present in the equilibrium mixture. Thus it is inferred that the basic stoichiometry is as indicated, at all temperatures investigated.

For the straight chain alcohols, plots of logK vs 1/T indicated straight lines from which estimation of heat of reaction could be made. Data taken with secondary and tertiary alcohols, while indicating the same general trends was erratic and cannot be used for other than qualitative estimation of trends. From heat of reaction data and values of the constants, estimations were made of heat of formation and standard molal entropy of the nitrite esters. These data are tabulated in Table 5.

Table 5....Indicated equilibrium constants for the reaction $2NO_2+ROH=HNO_3+RONO$ assuming the indicated stoichiometry.

Alcohol	K (mm^{-1})			Heat of Reaction	Nitrite Properties	
	25°C	40°C	55°C	Kcal/gmol	H_f	S
Methyl	1.60	0.31	0.10	-17.8	-17.06	65.4
Ethyl	0.91	0.145	0.032	-22.1	-28.58	61.8
n-Propyl	1.03	0.16	0.025	-24.1	-37.00	62.8
n-Butyl	0.54	0.072	0.010	-26.3	-45.26	67.6
n-Amyl	0.24	0.026		-27.9	-53.8	73.0
i-Propyl	0.27	0.15	0.03			
sec-Butyl	0.8	0.06	0.02			
t-Butyl	0.059	0.022	0.0035			

The properties of the nitrites while showing good agreement for methyl with the data of Leermakers (2) (17.06 as compared with 16.75 for heat of formation, and 65.4 compared with 65.2 for standard molal entropy), indicate serious deviations from expected values for the higher nitrites. Values of entropy are 6 to 10 units less than would be indicated by statistical computations.

Measurement was such that deviations could at most cause an error on one entropy unit. Effects due to structural isomerism (3) can be shown to have effects considerably less than the 6 to 10 units deviation in S. The constancy of K as computed indicates that no serious deviation from the basic stoichiometry could have occured, but does not preclude small deviations due to association, adsorbtion effects etc which would have the effect of varying concentrations in such a manner that K would be affected similarly at all equilibrium compositions.

Experimental heats of reaction are higher than expected. Thus experimental K's at 25 and 40° are high with respect to those at 55°C, indicating higher extents of reaction than would be expected. Association, adsorbtion etc involving reactants would with the extents of reaction noted tend rather to limit equilibrium extent of reaction and cannot explain the effects noted. Thus only product association offers a tenable explanation.

(2) J. Leermakers and H.C. Ramsperger, JACS 54 1837(1932)
(3) P. Tarte, Bull. Soc. Chim. Belg. 60 240(1951)

If association between products of the form, $HNO_2 \cdot RONO = K_x$ with an equilibrium equilibrium constant of 0.1 being assumed, the ratio of the true constant for the over all reaction to the constants as given in Table 5 are 0.83 when NO_2 reacted is 1.0mm, and 0.77 when NO_2 reacted is 3.0. These extents of reaction represent values near to the extremes of concentration used in this work and the deviation (4% from the mean value) is of the order of the precision with which the data was taken. Association will become less at higher T. If assumed negligible at 35°C and a value of 80% of the constant at 25° is assumed, heat of reaction is indicated to be some 1800calories less than tabulated in Table 7, and absolute entropy of the nitrite is some 6 units higher. It is thus postulated that product association to the extent of about 20% of the product formed takes place and is a cause for the unusually low values of ΔH_{RONO} indicated in this work.

Nitrite-Nitric Acid association is not unexpected inasmuch as HNO_3-RONO-ROH solutions in the liquid phase have been shown to be singularly unreactive with respect the the oxidations expected. Nitrite esters appear to be oxidation inhibitors in such solutions.

DISCUSSION

Results indicate that vapor phase rate amounts at most a few percent of the overall rates observed and is of negligible in this work. It has further been found that surface rate follows an equation of the form:

$$-dNO_2/dt = \frac{(k_s K_A K_1 S/V)(1 + 0.8 Z)(NO_2^2 \, ROH - Z^2/K)}{(1 + K_A ROH)}$$

where Z denotes mm NO_2 reacted.

Adjacent site surface controlled mechanism indicates that the denominator should enter to the second power, while adsorbtion rate controlling mechanisms indicate numerator dependances not in accord with experimental findings. Thus it is postulated that NO_2 (N_2O_4) reacts directly with adsorbed alcohol without itself first adsorbing. It is possible to postulate that NO_2 associates with already adsorbed alcohol and then reacts with NO_2 directly from the vapor phase, a mechanism indicating a rate law of the form

$$-dNO_2/dt = (k_s K_A K_2 \, NO_2^2 \, ROH \, S/V)(1/(1 + K_A ROH)(1 + K_B NO_2)$$

for intial conditions. In order that the second order behavior with respect to NO_2 be accounted for, K_B must be of the order of 0.01 and must show a heat of association or adsorbtion above 8 to 10 Kcal. These values are possible and such a mechanism cannot be discarded at this time.

Heats of adsorbtion were found to be of the order of magnitude of heats of vaporization. Coupled with the induction effects noted, this implies that reaction takes place with the essentially liquid phase outer adsorbed monolayers of alcohol. Heats of adsorbtion were significantly higher for secondary and tertiary alcohols than for the primary while the reverse trend was noted in the magnitude of the constants. Thus a significant difference exists in entropy of adsorbtion for primary alcohols as compared to other types.

Surface rate constants and energy quantities are very similar for all alcohols,

Secondary Butanol and Ethanol showing some exception. As H_A for sec-Butanol was determined from only two values of K_A, deviation may be caused by experimental error. Values of heat of adsorbtion for ethanol appear low, but no explanation can be found for this behavior at this time.

The work of Fairlie, Carberry and Treacy (1) was done in a reactor with S/V = 0.3. Extrapolation of the present data to this S/V indicates that specific rate constants of the order of 0.1 should have been noted instead of the 0.03 reported (methanol). Further, deviations from first order in alcohol should have been noted. In the previous work, the measurement light beam passed 5mm from the wall. The reported rates represent a mixture of free communication effects (considering the light beam as a reaction cell) and convection-diffusion from the vapor phase to the walls. The situation is complex and no doubt masked deviations in alcohol order. The data in all probability have little significance except for use in design of large size reactors. Time dependance in the autocatalytic effect may be attributed to diffusion-convection effects. In the present work, mass transfer effects are at best small due to the reactor size used and the fact that the measurement beam was of cell diameter. Diffusional gradients in the present work were approximately 10 times those of the previous workers.

The autocatalytic effect noted cannot be considered to be due to adsorbtion rate phenomena, for the same increases in rate were noted with very considerably different initial amounts of intial reactant charged, with attendant differences in partial pressure and time to achieve this condition. Work in this laboratory indicates that while NO_2, RONO, H_2O and nitrites in the feed charge had little effect on intial rate, 0.5mm HNO_3 increased rates observed by 50%. As 0.5mm corresponds to 1.0mm NO_2 reacted, the catalytic effect of HNO_3 alone account for 65% of the observed autocatalytic effect. The balance may be accounted for if it be assumed that Nitrite-HNO_3 associations complexes are also catalytic to the reaction. At the present time it is not known if this autocatalysis is a wall effect or if it represents a vapor phase catalytic rate.

Since both rate and equilibrium conversion are seriously reduced by increased Temperature, practical use of this reaction will be limited to lower temperatures. Surfaces inert to chemical attack (Teflon, Aluminum) while showing reduced rates of reaction, are indicated to be serviceable for use in running the reaction.

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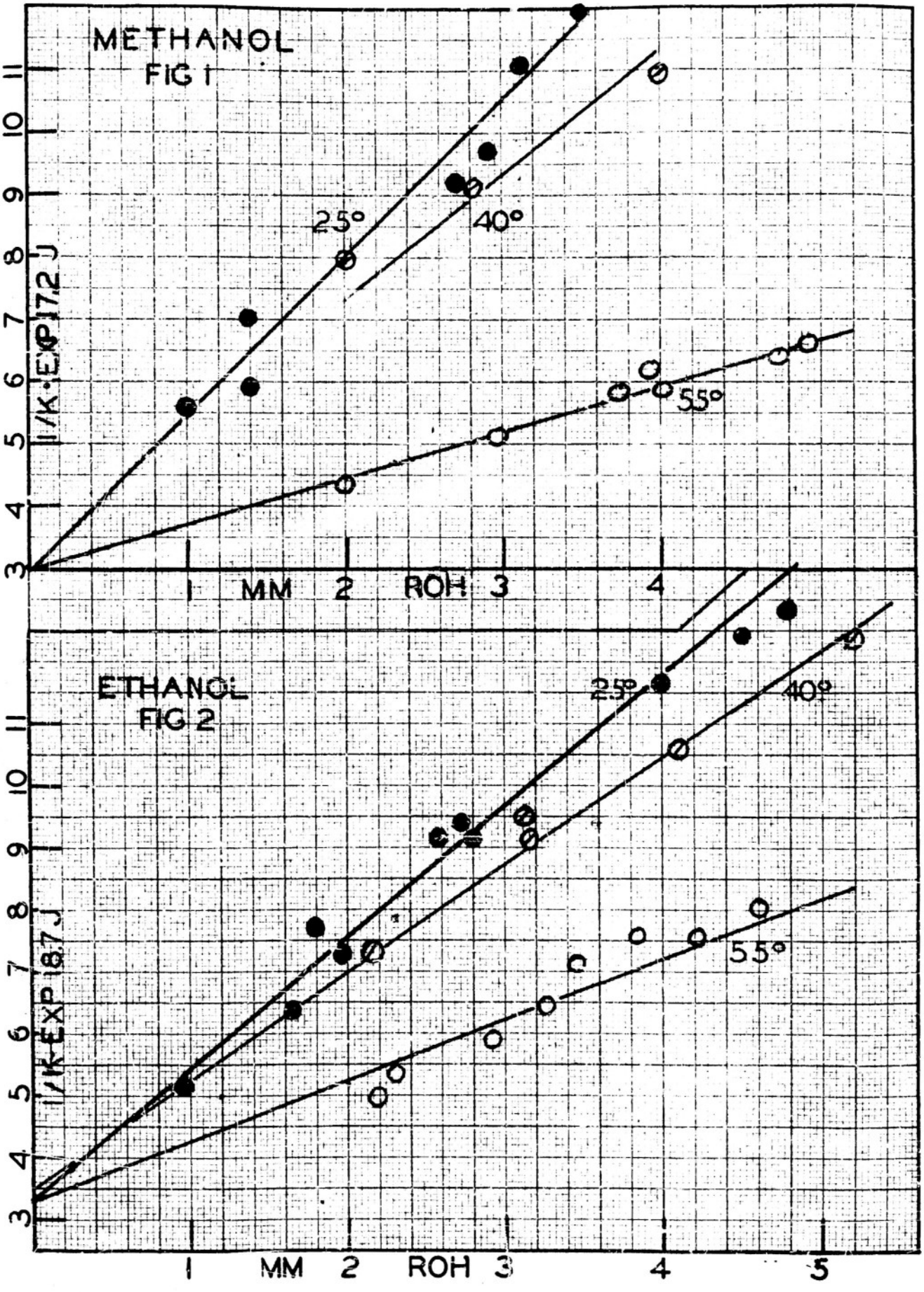

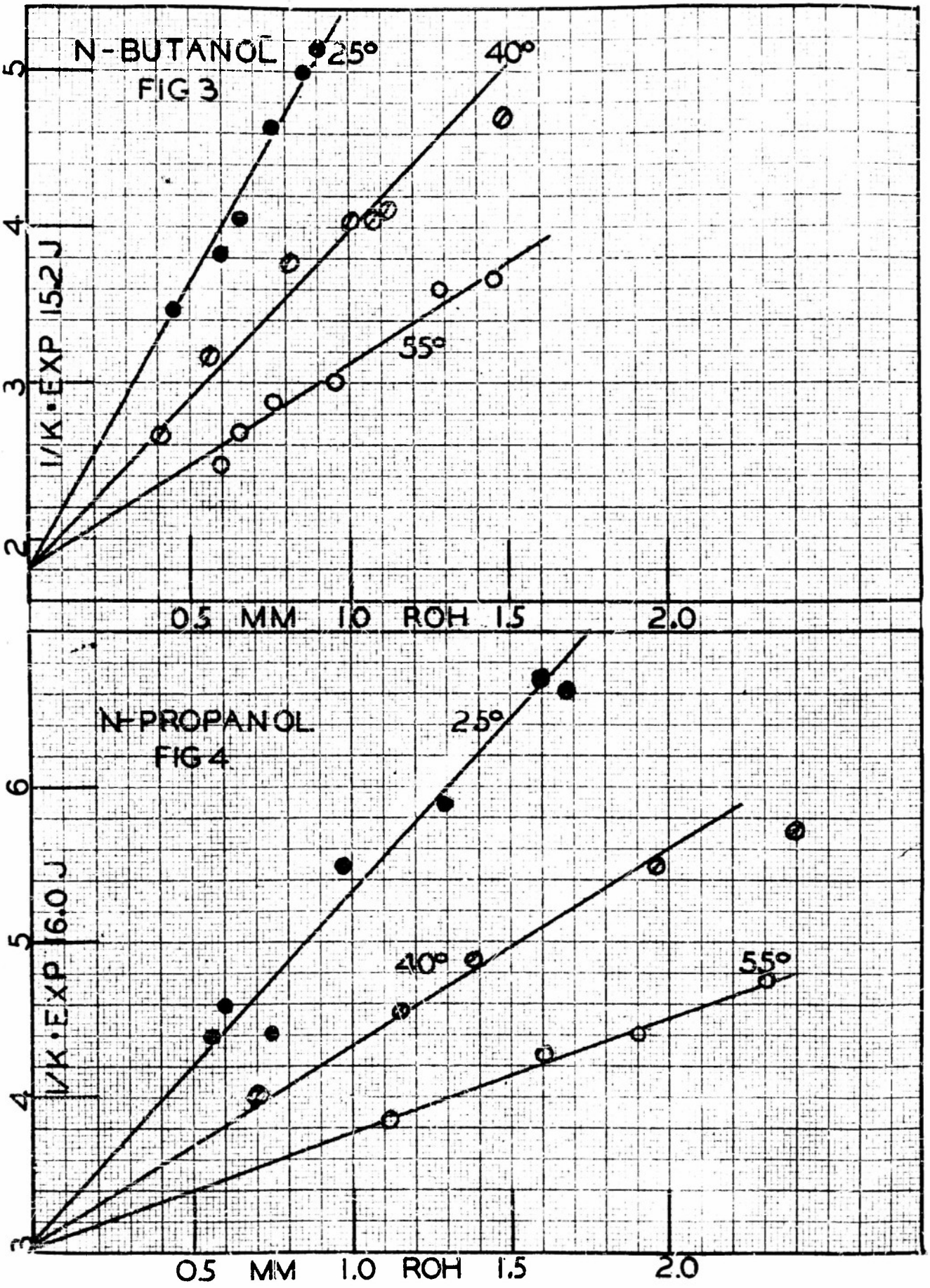

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