

The Inhibition of Homogeneous Organic Decompositions

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have some sort of tetrahedral symmetry about the carbon atom holding the I. In a surface both the C_2H_5 group and the I because of space occupation might be expected to orient outward. Since linkage on condensation will presumably occur with the one of the two hydrogens of the carbon atom attaching to the iodine atoms at the surface, a negative charge on the ion will facilitate such combination. Aniline was found to have negative sign preference. Toluene and chlorobenzene were also observed to favor the negative ion. These three substances are characterized by organic chemists as being strongly *ortho-para* directive and it may be that this tendency is also manifested in the condensation process. It is, however, more profitable to speculate further as follows:

The structure of aniline is pyramidal and presents many possible methods of combination. The bulky C_6H_5 group might be thought of as projecting outward from the surface in which case it is possible that the C_6H_5 may be the linking group. However, the fact that hydrogen bond formation is possible makes it more likely

that the N atom is outward in the droplet surface with the protons of the NH_2 inward. Then the hydrogens of the NH_2 of the condensing molecules which will be oriented downward by the field of a negative ion will favor linkage of the H with the nitrogen at the surface.

c. Positive sign preference

Perhaps the greatest difficulty at first encountered in interpreting these phenomena came in the behavior of the alcohols and fatty acids. On the basis of the action of H_2O the alcohols should be expected to show negative sign preference. Reflection will at once show why this is not the case. Hydrogen bond linkage is active here. However, the alcohols will orient with the organic radical or carbon chain outward where possible. In this case it is clear that the negative oxygen will point inward while the carbon chain and the H group are oriented outward. Thus the linkage will be facilitated by condensation on the positive ion, which orients the oxygen group of the approaching vapor molecule downward favoring hydrogen bond formation.

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The Inhibition of Homogeneous Organic Decompositions

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A free radical mechanism is proposed to account for the inhibition of organic decompositions by nitric oxide, based on the assumption that the nitric oxide can both start and stop reaction chains in the substrate. Propylene inhibits organic decompositions and a free radical mechanism appears to account for this effect also. Ethyl nitrite completely inhibits the oxygen promoted chain in acetaldehyde at 300°C but has only a relatively small effect at 500°C.

(1) INTRODUCTION

A FREE radical mechanism such as that proposed by one of us¹ leads to the conclusion that two organic compounds when mixed do not decompose independently of each other and consequently we would expect the experimental

result that the rate of decomposition of a particular compound would be either accelerated or retarded by addition of another compound. Acceleration of reaction rate has been observed in a large number of examples² but retardation of the rate is much less common; Hinshelwood and his co-workers have found that nitric oxide inhibits

¹ (a) Rice, J. Am. Chem. Soc. **53**, 1959 (1931); (b) Rice and Herzfeld, *ibid* **56**, 284 (1934); (c) Rice and Rice, *The Aliphatic Free Radicals* (The Johns Hopkins University Press, 1935).

² (a) Frey, Ind. Eng. Chem. **26**, 200 (1934); (b) Sickman and Allen, J. Am. Chem. Soc. **56**, 1251 (1934); (c) Echols and Pease, J. Am. Chem. Soc. **58**, 1317 (1936).

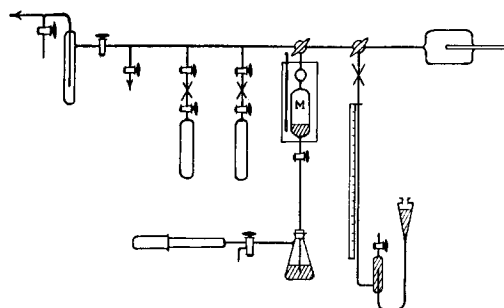


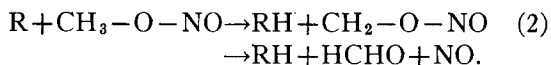
FIG. 1.

the decomposition of some organic compounds but not others³ and sometimes the products of a reaction have a slight but definite retarding influence.⁴

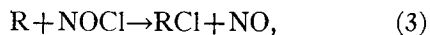
On the basis of our work in this laboratory we have concluded that, from the chemical standpoint, retardation of the rate of a reaction can occur in two ways according to the nature of the added material. In the first way it probably combines or reacts with the chain radicals to produce molecules³ according to the equation,



We have found that alkyl nitrites also show inhibition which may be ascribed to a dual action:



The molecules themselves inhibit and also the nitric oxide produced inhibits according to Eq. (1). On the other hand, earlier experiments^{1(c)} in this connection showed that nitrosyl chloride did not slow up the reaction rate of butane⁵ and certain other organic compounds; possibly the reaction,



requires too high an activation energy for nitrosyl chloride to be an effective inhibitor.

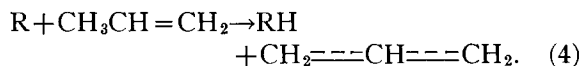
The second kind of inhibition may occur when the addition of a second substance causes the substitution, in greater or less degree, of the chain radical by another radical which is not so efficient for continuing the chain process. We

³ This work is summarized by Staveley and Hinshelwood, *J. Chem. Soc.* 1568 (1937).

⁴ Hinshelwood, *Proc. Roy. Soc. A* **114**, 84 (1927).

⁵ Compare Echols and Pease, *J. Am. Chem. Soc.* **59**, 766 (1937) who found that NO inhibits the butane decomposition.

have found that propylene inhibits the decomposition of hydrocarbons, ethers, acetone and acetaldehyde. The action is probably due to replacement of the chain carrier R by the allyl radical according to the equation,



The addition of propylene therefore is an example of the second kind of inhibition since probably the allyl radical is not a very efficient chain carrier as compared with methyl or ethyl radicals which are the most common carriers in the above reactions.

The addition of small quantities of either nitric oxide, alkyl nitrites or propylene, to a paraffin hydrocarbon or an ether, causes usually a reduction in rate which is very marked with nitric oxide; in all cases the rate diminishes, rapidly at first until a point is reached where further additions have very slight effect.⁶ On the other hand, in the case of acetone or acetaldehyde, there is a sharp contrast between the action of nitric oxide or alkyl nitrites and propylene. Whereas propylene has the normal inhibiting effect, nitric oxide or alkyl nitrites do not show any inhibition.

From the kinetic standpoint no such difference would be expected for the different inhibitors if we assume that the effect of all of them is, essentially, to reduce the concentration of the chain radicals. The disagreement in our experimental results between the action of propylene and the other two inhibitors, indicated the desirability of studying the efficiency of chain breaking in the temperature range 500–550°C, in which many organic compounds decompose at a conveniently measurable rate.

TABLE I. *Effect of small quantities of O₂ and ethyl nitrite on acetaldehyde at 300°C. Acetaldehyde pressure = 380 mm.*

I mm O ₂	II mm EtONO	III λ	IV Error
0.17	0	94	±12
0.34	0	68	± 5
0.94	0	37	± 2
0	0.19	0	±10
0	1.04	0	± 2
0	1.05	0	± 2
0	1.05	0	± 2

⁶ Very large addition of NO causes oxidation. See Section (4) and reference 3.

(2) EXPERIMENTAL

The work described in this paper was done in a static system and the rate was followed manometrically. Fig. 1 shows a sketch of the apparatus. The reaction vessel consisted of a 200 cc transparent silica bulb which fitted in a furnace constructed of a graphite cylinder surrounded completely by thin Nichrome sheet to prevent oxidation. The graphite cylinder was heated electrically and lagged in the usual manner and gave a uniform temperature inside our reaction bulb to $\pm 1^\circ\text{C}$.

The mixing bulb, *M*, is the most significant part of the apparatus. Using this bulb we could make up accurately known mixtures and displace the whole of the gas into the furnace. This gave us a method of measuring P_0 by displacing an equal volume of a nonreactive gas from the mixing bulb to the furnace, the initial and final conditions of temperature and pressure being the same as with the substrate. Since we were interested in measuring the expansion caused by an initial very rapid reaction, an accurate estimate of P_0 was essential and we prefer the displacement method to one of connecting the mixing bulb with the empty reaction bulb and measuring the initial and final pressure in the mixing bulb. If this method is used, it should be noted that the pressures in the mixing bulb and reaction bulb should not be allowed to equalize because the reaction mixture expands very rapidly during the first few seconds and some of the partly decomposed gas may be driven back into the mixing bulb.⁷

The manifold accommodates two sample bulbs,

TABLE II. *Inhibition of the oxygen promoted chain decomposition of acetaldehyde by ethyl nitrite. Temperature = 300°C. Pressure CH₃CHO = 380 mm.*

I mm O ₂	II mm EtONO	III λ	IV Error
0.47	1.05	0	± 4
1.05	2.1	0	± 2
0.94	0.49	27	± 2
0.94	1.0	0	± 2
0.94	1.9	0	± 2
0.94	2.8	0	± 2
0.17	0.37	0	± 12
0.34	0.70	0	± 6

⁷ Equalization of pressure is satisfactory if there is no rapid initial rate and has been used by Schultz and Kistiakowsky, J. Am. Chem. Soc. **56**, 395 (1934).

TABLE III. *Effect of small quantities of oxygen or ethyl nitrite on acetaldehyde. Temp. = 502°C. Acetaldehyde pressure = 500 mm.*

I mm O ₂	II mm EtONO	III λ	IV Error
0.24	0	555	± 8
0.27	0	520	± 7
0.62	0	269	± 3
0.225	0	606	± 9
0	0.66	24	± 3
0	1.28	15.6	± 2
0	2.7	6.7	± 1

one containing the substrate and the other the inhibitor; it is also fitted with a McLeod gauge and is connected to a pumping system consisting of a two-stage mercury vapor pump backed by an oil pump.

(3) INHIBITION WITH ETHYL NITRITE

The first series of experiments described in this section was performed at 300°C with acetaldehyde. Pure acetaldehyde is stable at this temperature and gave no initial increase in pressure; the measured P_0 using acetaldehyde was the same as that obtained by using the same amount of an inert gas after correcting for gas law deviations. However, if the acetaldehyde is mixed with small measured quantities of oxygen (0.1–0.3 percent) in the mixing bulb and then transferred to the reaction bulb, there is considerable decomposition of the acetaldehyde, far more than could be accounted for on the basis of simple oxidation; the decomposition is completed in the first few seconds before any measurements could be made and was measured by the difference in the observed and calculated P_0 , after making a small correction for the added oxygen. The number of acetaldehyde molecules decomposed per molecule of oxygen (λ) was calculated on the assumption that the acetaldehyde decomposed into two product molecules.

The results of our experiments are shown in Table I; since the value of λ depends on the difference of two pressure measurements, the error will vary considerably and we have therefore included in column IV, values for the error in λ assuming that the difference between the calculated and measured pressure is subject to an error of ± 2 mm. Table I also contains some measurements on acetaldehyde containing small

TABLE IV. *Inhibition of the oxygen promoted chain decomposition of acetaldehyde by ethyl nitrite at 502°C. Acetaldehyde pressure = 500 mm.*

I mm O ₂	II mm EtONO	III λ	IV Error
0.23	0.24	496	± 9
0.23	0.51	440	± 9
0.23	0.93	379	± 9
0.225	0.94	361	± 9
0.23	1.72	283	± 9
0.24	2.55	267	± 9
0.23	2.95	217	± 9
0.225	3.3	209	± 9
0.225	4.9	205	± 9
0.225	8.5	227	± 9

quantities of ethyl nitrite. The ethyl nitrite had no detectable effect either by inducing an initial rapid acceleration or any subsequent decomposition. Except for a small correction for the decomposition of the nitrite, the mixture behaved like pure acetaldehyde.

In Table II we show the results for mixtures of ethyl nitrite and oxygen with acetaldehyde; within the limits of our measurement, the ethyl nitrite inhibits the oxygen induced chain completely if its concentration is equal to or greater than that of oxygen.

These results are similar to those obtained by Mitchell and Hinshelwood,⁸ who found that at 300°C, chains induced photochemically in acetaldehyde could be shortened from over 100 to 1 by the addition of small quantities of nitric oxide.

We then performed a second series of experiments exactly similar to the first but at 500°C. Since acetaldehyde decomposes at a slow but measurable rate at this temperature, it was necessary to make an additional correction for its decomposition. This was done by plotting the pressure-time curve and extrapolating back to zero time. The difference between this P_0 and the calculated P_0 (obtained from the pressure measurement in the mixing bulb) gave the amount of induced decomposition; a small correction was necessary to take care of the oxygen or ethyl nitrite added. The results obtained when acetaldehyde is mixed with either oxygen or ethyl nitrite are shown in Table III. The chain length of the oxygen sensitized reaction is greatly increased and in addition a new phenomenon appeared in the experiments with ethyl nitrite

⁸ Mitchell and Hinshelwood, Proc. Roy. Soc. **A159**, 32 (1937).

TABLE V. *Decomposition of acetaldehyde in presence of small amounts of nitric oxide. Temp. = 478°C. Initial pressure acetaldehyde = 250 mm.*

Press. NO $100 \times (dp/dt)_0 \div P_0$	0	0.6	1.2	2.4	6.1	12.0
	1.60	1.79	2.05	2.28	3.30	3.83

Pressures in mm Hg., time in min.

since it actually induced a short chain decomposition in the aldehyde. The effect of mixtures of oxygen and ethyl nitrite on the decomposition is shown in Table IV.

The results show that ethyl nitrite is a very inefficient inhibitor at 500°C as might be expected from the experimental result that ethyl nitrite itself actually induces short chains in acetaldehyde. The effect of ethyl nitrite on the oxygen induced chain is to reduce the length to a minimum value of about two-fifths, when the ethyl nitrite is present in about tenfold excess over the oxygen. Addition of one molecule of nitrite per molecule of oxygen has very little effect on the chain length at 500°C although at 300°C there is complete inhibition.

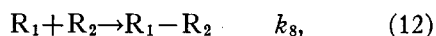
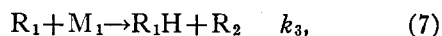
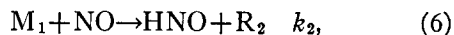
In view of these experimental results it seemed desirable to examine the effect of small quantities of pure nitric oxide on the rate of decomposition of acetaldehyde in the neighborhood of 500°C especially since our method would show up any rapid initial acceleration that occurred. We did not find any such effect as in the case of ethyl nitrite but we did however find that even very small amounts of nitric oxide accelerated the rate of decomposition of acetaldehyde. The results of these experiments are shown in Table V and prove that quantities of nitric oxide of less than 0.5 percent accelerate the reaction rate appreciably at 478°C.

(4) DISCUSSION OF NITRIC OXIDE INHIBITION

It seems reasonable to conclude from our experimental results that nitric oxide can both start and stop chains when introduced into acetaldehyde. This is probably true also for other organic compounds and the following mechanism⁹ may be proposed for decompositions in presence of nitric oxide.¹⁰

⁹ See in this connection reference 1 (c), pp. 86-90.

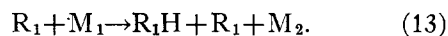
¹⁰ When large amounts of nitric oxide are present, a complicated oxidation process predominates. See Gay and



$[M_1] = x_1$, $[NO] = y$, $[R_1] = x_2$, $[R_2] = x_3$, k_1x_1 and $k_6x_2^2$ are the respective rates for the appearance and disappearance of *one* radical. According to this, organic compounds decompose in two ways according as the chain ends by reactions (9) and (10) or reactions (11) and (12).

Scheme I

In this scheme reaction (8) has a very low activation energy, so that x_3 may be neglected and Eq. (7) written,



Acetaldehyde follows this scheme and reaction (7) in this case would be,



Since R_2 is present in very low concentration, the chain must end by reactions (9) and (10). Setting up the usual steady state conditions and solving for x_2 we obtain:

$$k_1x_1 + k_2x_1y = k_5x_2y + k_6x_2^2 \quad (15)$$

$$x_2 = -(k_5/2k_6)y$$

$$+ [(k_1x_1 + k_2x_1y)/k_6 + k_5^2y^2/4k_6^2]^{\frac{1}{2}}. \quad (16)$$

If the chain length is greater than 10, the rate of the reaction is given by,

$$dx_1/dt \cong k_3x_1x_2,$$

and if the concentration of nitric oxide is very small this becomes,

$$\frac{dx_1}{dt} = k_3x_1 \left[\left(\frac{k_1x_1 + k_2x_1y}{k_6} \right)^{\frac{1}{2}} - \frac{k_5}{2k_6}y \right]. \quad (17)$$

Travers, *Nature* (a) **137**, 906 (1936); (b) **138**, 546 (1936). Our mechanism applies only when the NO concentration is sufficiently small that this is negligible.

As the concentration of nitric oxide increases we have,

$$dx_1/dt \cong k_3x_1[(1/k_5)(k_2x_1 + k_1x_1/y)] \quad (18)$$

and finally at higher values of y ,

$$dx_1/dt \cong k_2k_3x_1^2/k_5. \quad (19)$$

Scheme II

In this scheme reaction (8) has a high activation energy and Eqs. (11) and (12) represent the chain terminating reactions. We then have,

$$k_1x_1 + k_2x_1y = k_7x_3y + k_8x_2x_3, \quad k_3x_1x_2 = k_4x_3,$$

$$x_2 = -k_7y/2k_8$$

$$+ [(k_1k_4 + k_2k_4y)/k_3k_8 + k_7^2y^2/4k_8^2]^{\frac{1}{2}}. \quad (20)$$

For small concentrations of nitric oxide, we have,

$$\frac{dx_1}{dt} = k_3x_1 \left[\left(\frac{k_1k_3x_1 + k_1k_4y}{k_3k_8} \right)^{\frac{1}{2}} - \frac{k_7}{2k_8}y \right] \quad (21)$$

and for large concentrations

$$dx_1/dt \cong k_2k_4x_1/k_7. \quad (22)$$

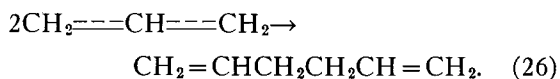
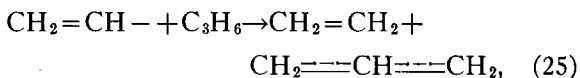
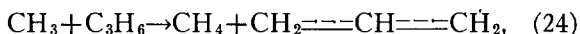
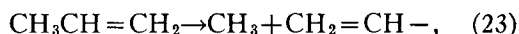
It seems unwise at present, to attempt an exact discussion of the application of these mechanisms to the phenomenon of inhibition by nitric oxide, because we are uncertain as to what extent the oxidation reaction affects the experimental results. Indeed Verhoek found¹¹ that the decomposition of acetone by nitric oxide at 600°C was predominantly an oxidation process. However, it is clear that the addition of small quantities of nitric oxide would be expected first to diminish the rate until finally further additions would have no effect. This relation³ has been found for a number of organic compounds. Furthermore the inhibiting effect of the nitric oxide should increase as the concentration of substrate diminishes according to scheme I whereas according to scheme II the inhibiting effect would be independent of the substrate concentration. Propaldehyde, butaldehyde and ethane behave³ according to scheme I whereas dimethyl ether and diethyl ether behave³ according to scheme II; this is what may be expected for the aldehydes and ethers but not for ethane which is exceptional in that it should fall into scheme II.

¹¹ Verhoek, *Trans. Faraday Soc.* **31**, 1534 (1935).

(5) INHIBITION WITH PROPYLENE

The peculiar effect of propylene on organic decompositions was discovered accidentally in the course of some experiments in which we were trying to catalyze decompositions by adding small amounts of cyclopropane. We were testing to see if the cyclopropane ring would open, thus supplying radicals which would be expected to accelerate the rate. Instead, the rate decreased considerably and further investigation showed that this effect was most probably due to propylene into which cyclopropane isomerizes on heating.¹²

The decomposition of pure propylene was first investigated by heating it in a 12-liter Pyrex flask at 530°C, and pumping out and analyzing the products; the initial pressure was 334 mm and after 40 min. the pressure had only increased by 3 mm. About 15 percent of the propylene had decomposed, giving equal quantities of ethylene and methane and a smaller amount of a C₆ hydrocarbon which was not identified. We assume that the mechanism of the propylene decomposition is,

TABLE VI. *Effect of propylene on rate of decomposition.*

SUBSTRATE	TEMP. °C	P ₀ SUB-STRATE	P ₀ PRO-PYLENE	100 × (dp/dt) ₀ ÷ P ₀
Propane	497	204	0	0.57
Propane	497	204	102	0
n-Butane	512	290	0	1.1
n-Butane	512	290	13	0.8
n-Butane	512	290	25	0.57
n-Butane	512	290	53	0.53
n-Butane	512	290	102	0.27
n-Butane	512	290	107	0.33
n-Butane	512	290	163	0.17
Acetaldehyde	500	206	0	5.1
Acetaldehyde	500	201	102	2.3
Acetone	550	182	0	5.5
Acetone	550	150	50	1.6
Acetone	550	137	54	1.5
Dimethyl ether	508	203	0	3.4
Dimethyl ether	508	199	108	1.0
Trimethyl amine	470	203	0	7.5
Trimethyl amine	470	194	103	4.3
Ethylene oxide	408	405	0	0.72
Ethylene oxide	408	465	104	0.09

¹² Trautz and Winkler, J. prakt. Chem. 104, 53 (1922).

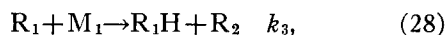
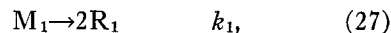
This would lead to no change in pressure for the decomposition and appears to account satisfactorily for the products. Propylene is appreciably more stable than the organic molecules whose decomposition it inhibits.

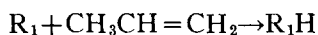
We have completed only some preliminary experiments on the effect of propylene in which we have varied the substrate, and in one example the concentration of the propylene also. The results obtained are shown in Table VI.

We did not continue with this phase of the experimental work because our apparatus was not adapted to measuring rates of reaction in the very early stages. After a few percent decomposition has occurred, the reaction becomes very complex because the substrate frequently yields propylene or some other unsaturated molecule which can inhibit and the decomposition of the propylene yields presumably diallyl which would be expected to diminish the inhibiting effect of the propylene by easily dissociating into allyl radicals. A further difficulty lies in the fact that minute traces of oxygen exert a profound effect on the initial rate of decomposition and it seemed best to examine the oxygen effect before continuing this investigation.

(6) DISCUSSION OF INHIBITION BY PROPYLENE

We shall assume that propylene is sufficiently stable as compared with the substrate molecules investigated, that we can neglect any radicals produced by its decomposition according to Eq. (23). The effect of propylene is to remove some of the chain radicals R by reacting to give RH and the allyl radical which combines with itself to form diallyl instead of continuing the chain. We shall also neglect any chain propagation by the allyl radical. Essentially the propylene functions as a third body for removing radicals, and other unsaturated molecules might be expected to act similarly.¹³ The following scheme may then be used to represent organic decompositions in presence of propylene:

¹³ Recently Staveley, Proc. Roy. Soc. A162, 557 (1937) has reported that ethylene inhibits the ethane decomposition.



$$[M_1] = x_1, \quad [R_1] = x_2, \quad [R_2] = x_3, \quad [\text{C}_3\text{H}_6] = x_0.$$

If the chain ends by (31) and (32) we have

$$k_6 x_2^2 + k_5 x_2 x_0 - k_1 x_1 = 0; \quad (33)$$

$$\therefore x_2 = [k_1 x_1 / k_6 + k_5^2 x_0^2 / 4k_6^2]^{\frac{1}{2}} - k_5 x_0 / 2k_6. \quad (34)$$

If the chain length is greater than 10 (at maximum inhibition),

$$dx_1/dt \cong k_3 x_1 x_2$$

$$= x_1^{\frac{1}{2}} k_3 \left(\frac{k_1}{k_6} \right)^{\frac{1}{2}} \left[\left(1 + \frac{k_5^2 x_0^2}{4k_1 k_6 x_1} \right)^{\frac{1}{2}} - \left(\frac{k_5^2 x_0^2}{4k_1 k_6 x_1} \right)^{\frac{1}{2}} \right]. \quad (35)$$

The corresponding equation for the chain ending by (30) and (32) is,

$$dx_1/dt \cong k_3 x_1 x_2$$

$$= x_1 \left(\frac{k_1 k_3 k_4}{2k_8} \right)^{\frac{1}{2}} \left[\left(1 + \frac{k_4 k_5^2 x_0^2}{8k_1 k_3 k_8 x_1^2} \right)^{\frac{1}{2}} - \left(\frac{k_4 k_5^2}{8k_1 k_3 k_8} \right)^{\frac{1}{2}} \frac{x_0}{x_1} \right]. \quad (36)$$

The decomposition of *n*-butane follows Eq. (35) if as seems probable, the large chain radicals are very unstable. Writing

$$y = (k_5^2 x_0^2 / 4k_1 k_6 x_1)^{\frac{1}{2}}. \quad (37)$$

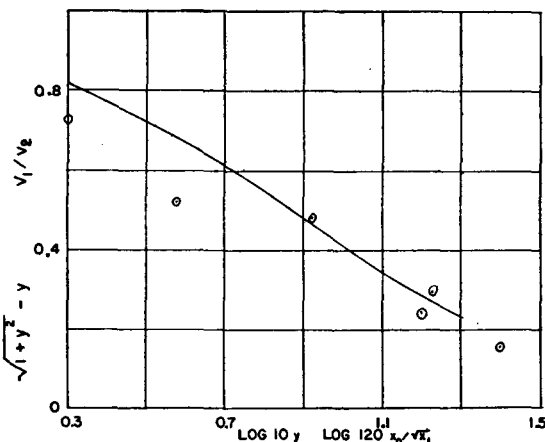


FIG. 2. Inhibition of *n*-butane decomposition by propylene. The curve is obtained by plotting $\log 10 y$ against $(1+y^2)^{\frac{1}{2}} - y$. The points are experimental (Table IV) and are obtained by plotting $\log 120(x_0/(x_1)^{\frac{1}{2}})$ against the ratio of the inhibited to uninhibited reaction (V_1/V_2); x_0 and x_1 are the concentrations of propylene and butane, respectively, relative to normal pressure and temperature (reference 1(b)).

The inhibition for constant substrate concentration may be represented by a plot of y against $(1+y^2)^{\frac{1}{2}} - y$. This is shown in Fig. 2 which also contains the experimental points taken from Table IV. This gives a value for

$$(k_5^2 / 4k_1 k_6)^{\frac{1}{2}} \cong 10$$

assuming an activation energy corresponding to k_5 of 22 cal. which seems reasonable. E_1 was taken as 65.4 cal.¹⁴ and E_6 as 8 cal.^{1(b)}

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¹⁴ Rice and Johnston, J. Am. Chem. Soc. **56**, 214 (1934).