

together with reactions 3 and 21. In terms of the reaction kinetics,  $G(\text{H}_2)$  is given by the relationship

$$G(\text{H}_2) = G^{\text{M}}(\text{H}_2) + \left\{ G(\text{H}^\alpha) + \frac{G(\text{e}_{\text{aq}}^-)}{1 + (k_{21}(\text{CH}_3\text{CHO})/k_3(\text{H}^+))} \right\} P$$

where

$$P = \frac{k_{23} + k_{25}([\text{CH}_3\text{CH}(\text{OH})_2]/[\text{CH}_3\text{CHO}])}{k_{23} + k_{24} + k_{25}([\text{CH}_3\text{CH}(\text{OH})_2]/[\text{CH}_3\text{CHO}])}$$

and is constant at constant temperature.

The rate constant ratio for reactions 3 and 21, calculated from the values of  $k_3/k_6$  and  $k_6/k_{21}$ , is  $k_3/k_{21} = 1.69$ . Values of  $G(\text{e}_{\text{aq}}^-)$  may be determined from the  $G(-\text{H}_2\text{O})$  yields shown in Fig. 2. The constant,  $P = 0.87$ , represents the fraction of hydrogen atoms leading to hydrogen formation and was evaluated from data obtained at pH 1.20 where the influence of various additives, *i.e.*, acetic acid and 2-propanol, on  $G(\text{H}_2)$  were investigated. Substituting this information in the expression above we obtain a theoretical pH dependence for  $G(\text{H}_2)$  which, as can be seen from Fig. 3, agrees well with experimental findings.

### Conclusions

The radiation chemistry of the systems described above are readily interpreted on the basis of the primary formation of two reducing species,  $\text{e}_{\text{aq}}^-$  and  $\text{H}^\alpha$ .  $\text{H}^\alpha$  undergoes the reactions normally attributed to hydrogen atoms, *e.g.*, reactions 7, 15, and 24, and its identification as such is supported by the reaction kinetic studies of Rabani and Stein.<sup>16</sup> These hydrogen atoms may arise from the decomposition of excited molecules,<sup>7</sup>  $\text{H}_2\text{O}^*$ , formed either by ion recombination in the spurs or by the direct excitation of surrounding water molecules, or possibly from the spur

reactions 4 and 5.<sup>20</sup> However, the data presented above show that the yield of  $\text{H}^\alpha$  is unaffected by relatively high concentrations of electron scavengers such as  $\text{H}_3\text{O}^+$ ,  $\text{N}_2\text{O}$ , acetone, and acetaldehyde.

In systems containing  $10^{-2} M$  2-propanol and  $\text{N}_2\text{O}$  the yield of hydrated electrons in the bulk of the solution was found to be  $G(\text{e}_{\text{aq}}^-) = 2.80 \pm 0.1$  under neutral conditions of pH. Thus since  $\text{H}^\alpha$  is present in a yield of  $G(\text{H}^\alpha) = 0.60$ , these observations are consistent with the views expressed earlier by Rabani and Stein; *i.e.*, that  $G(\text{H}^\alpha)$  is actually  $3.40 \pm 0.15$  in aqueous 2-propanol and not 2.90 as has been generally accepted.

The results shown in Fig. 1 suggest that under similar conditions of pH the electron yield in the bulk of an  $\text{O}_2$ -saturated solution should be  $G(\text{e}_{\text{aq}}^-) 2.80 \pm 0.1$ , as was observed by Czapski and Allen<sup>18</sup> using the  $\text{O}_2$ - $\text{H}_2\text{O}_2$  system. This assumes, however, that the determining factor in the production of  $G 2.80$  electrons in the 2-propanol and 2-propanol- $\text{N}_2\text{O}$  systems is not scavenging of OH radicals by 2-propanol according to reactions 8 and 8a, which may not necessarily apply.

Czapski and Allen concluded from their results that the electron yield which they determined constituted all of the reducing species produced in the solution and thus challenged the existence of  $\text{H}^\alpha$  in oxygenated solutions. However, recent studies by Scholes, *et al.*,<sup>31</sup> using solutions of  $\text{O}_2$  and formate have shown that  $\text{H}^\alpha$  is formed in the presence of oxygen and enters into competing reactions with  $\text{O}_2$  and formate.

It seems fairly certain, therefore, that the two reducing species are formed in irradiated aqueous solutions although some questions remain concerning their respective yields. In particular, more investigations are necessary in order to elucidate the problems relating to oxygenated systems.

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## Studies with a Single-Pulse Shock Tube. III. The Thermal Isomerization of Methyl Isocyanide

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The thermal isomerization of methyl isocyanide to acetonitrile has been investigated behind reflected shocks over the temperature range 710–860°K. The heated mixture consisted of 2% methyl isocyanide in argon. The reaction products were analyzed by vapor phase chromatography. The first-order rate constants obtained in this temperature region are higher by a factor of about  $10^6$  when compared to the lower temperature ( $\sim 500^\circ\text{K}$ .) values. An Arrhenius extrapolation and Slater's equation for the dependence of  $(k/k^\infty)$  on temperature were used to compare the high with the low temperature data.

### Introduction

The thermal isomerization of methyl isocyanide has been studied recently by Schneider and Rabinovitch<sup>1</sup> over the temperature region 450–530°K. and over a wide range of  $(k/k^\infty)$ . These investigators also recently reported their work on the isomerization of methyl- $d_3$  isocyanide.<sup>2</sup> It was shown that the reaction is homogeneous and unimolecular. Owing to the relatively small number of degrees of freedom, the limiting first-order rate constant was reached only at pressures

of around 8 atmospheres; its value is

$$k_{\text{uni}}^\infty = 10^{13.6} \exp(-38,400/RT)$$

This paper is a continuation of our study of unimolecular reactions at the high temperatures attainable in shock tubes. Although the high pressure unimolecular limit could not be reached in the present glass shock tube, due to the excessive pressures which would be necessary, our data may be compared with those of Schneider and Rabinovitch by means of the equation given by Slater on the influence of temperature on  $(k/k^\infty)$ .

(1) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962).

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## Experimental

**Apparatus.**—The single-pulse shock tube which was used and the gas dynamic and experimental techniques have described in previous publications.<sup>3a,b</sup> The incident shock speeds were recorded, and from these the reflected shock temperatures were computed. The time intervals for the incident shock to travel between two pressure transducers varied between 116 and 126 mm./ $\mu\text{sec.}$ , and could be measured with the aid of 1- $\mu\text{sec.}$  time marks to  $\pm 1 \mu\text{sec.}$  Dwell times were read with an accuracy of 10%.

Owing to the relatively low activation energy for the isomerization reaction ( $\sim 35 \text{ kcal./mole}$ ), the temperature region which gave half-times of around 1 msec. is "very low" for reflected shock studies. Hence, helium was used as the driver gas; this permitted the tube to be "tuned" without unduly increasing the length of the driver section. The driven section was operated at  $p_1 \sim 150 \text{ mm.}$ , 0.5-mil mylar diaphragms were used. The driven section was pumped to about 1  $\mu$  and had a leak rate of about 1  $\mu/\text{min.}$

**Materials.**—Methyl isocyanide was prepared in a manner similar to that used by Schneider and Rabinovitch.<sup>4</sup> Silver cyanide and methyl iodide were shaken in a Pyrex bomb at 55° for 2 hr. Potassium cyanide and water were then added and the mixture was crudely distilled to separate the low boiling fractions. The distillate was then fractionally distilled. The isocyanide fraction was dried over magnesium sulfate and then vacuum distilled onto a liquid nitrogen-cooled cold finger. The resulting isocyanide was found by gas chromatography to contain 2% acetonitrile and 0.1% methyl iodide. The 2% acetonitrile left in the mixture was taken into account when rate constants were computed.

The acetonitrile used for calibration of the vapor phase chromatograph was Eastman chromatography grade. The argon used was Matheson pure grade, listed as 99.998%. Mixtures of methyl isocyanide in argon were prepared in 12-l. Pyrex bulbs and were thoroughly mixed before use.

**Analysis.**—The reaction products were analyzed with a Perkin-Elmer 154 vapor fractometer using a 6-ft. R column at 70° and a column pressure of 50 p.s.i.g. Helium was used as the carrier gas. Dependable analysis for methyl isocyanide was not possible due to its irreversible absorption on the column. (Other columns which were tested showed the same behavior.) The acetonitrile peak served for the computation of the reaction mixtures composition. First a calibration curve of peak areas vs. pressure for a mixture of 2% acetonitrile in argon was prepared. When the shocked gas was analyzed the absolute pressure introduced into the fractometer was measured, so that the peak area gave the absolute amount of acetonitrile present. From the initial composition of the shocked gas, the extent of reaction was computed. Since absolute, rather than relative amounts were measured, the calibration curve was checked before and after every few runs. The checks agree with the calibration curve to within 1%. This method of analysis is dependable provided no driver gas is trapped in the sample collected for analysis. No helium could be detected by mass spectrometric analysis of the shocked samples.

**Computations.**—Temperatures behind reflected shocks as a function of incident shock speeds were computed using the three conservation equations and the ideal gas equation of state. The computations were carried out on a CDC 1604. The Fortran program<sup>5</sup> directly computed the partition functions, as needed, from the molecular weights, moments of inertia, the fundamental frequencies of the methyl isocyanide, and the shocked gas composition. Since the thermodynamic parameters in the reflected shock have to be obtained by a trial and error procedure, the above method, which expresses vibrational enthalpies as Einstein functions, proved most convenient.

The exothermicity of isomerization (15 kcal./mole) was not introduced into the energy conservation equation but was taken into account, as previously,<sup>4</sup> by a correction factor for  $T_3$ .

**Quenching Rate.**—Owing to the low temperatures behind the reflected shocks, the cooling rates were lower ( $0.43 \times 10^6 \text{ deg./sec.}$ ) than the ones reported previously ( $1 \times 10^6 \text{ deg./sec.}$ ) for  $T_3$ 's around 1200°K.<sup>3a,b</sup> However, the rate at which the chemical reaction is quenched is given by the relation

$$\frac{d \ln k}{dt} = \frac{E_a}{R} \frac{1}{T_3^2} \frac{dT_3}{dt} \quad (1)$$

Since  $T_3$  was considerably lower than in our previous studies, the values of  $(1/T_3^2)(dT_3/dt)$  were about the same. Owing to the low activation energy for isocyanide isomerization, the quenching rate was lower by a factor of two. Table I summarizes these results for typical runs.

The contribution to the chemical reaction in the cooling phase was obtained by plotting the rate constant vs. time after the arrival of the cooling wave and was computed by the method given in part I of this series.<sup>3a</sup> It was found that effective dwell times were 10% greater than those directly recorded.

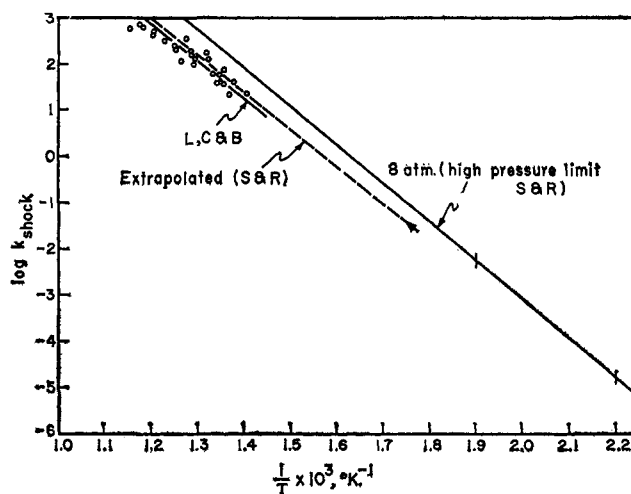


Fig. 1.—Arrhenius plots for the isomerization of methyl isocyanide. The heavy solid line is the line for  $k^\infty = 10^{13.4} \exp(-38,400/RT)$  as determined by Schneider and Rabinovitch. The temperature range of their experiments is indicated by the short vertical lines. The line marked L, C, and B is the median line for the shock tube data, while the dashed line is the extrapolated curve (S and R) assuming the argon collision efficiency was 5% of the  $\text{CH}_3\text{NC}$  collision efficiency.

## Results

Mixtures varying from 2.02 to 2.17% methyl isocyanide in argon were shock heated. Details of the experiments are given in Table II. The initial pressure in the driven section,  $p_1$ , varied from 120 to 200 mm. and compression ratios,  $p_6/p_1$ , between 3.22 and 3.94. The equivalent partial pressures of methyl isocyanide [ $p_1(\text{CH}_3\text{NC}) \times p_6/p_1$ ] behind the reflected shock ranged between 10.2 and 14.2 mm. The dwell times listed in column 7 of Table II were computed for the space average from the oscilloscope records by the method described in part I. These were increased by 10% to allow for the contribution from the cooling phase.

Owing to the large equilibrium constant of the reaction (around  $10^6$ ), the back reaction was neglected and the rate constants were calculated from the first-order relation

$$kt = -\ln \frac{a - x_t}{a - x_0} \quad (2)$$

where  $x_0$  is the initial concentration of acetonitrile,  $x_t$  is its concentration at time  $t$ , and  $a$  is the initial methyl isocyanide concentration plus  $x_0$ . These rate constants were plotted against the corrected reflected shock temperatures in Fig. 1. The median values as a function of temperature are indicated by the short solid line in that figure. Owing to the magnitude of the high pressure limit, shock data could not be obtained in the unimolecular range with the glass tube

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(5) The authors are indebted to Dr. Chava Lifshitz for invaluable help in writing the program.

TABLE I  
 TYPICAL QUENCHING RATES FOR THREE REACTIONS STUDIED IN A SINGLE-PULSE SHOCK TUBE

Reaction	$E_a$ , kcal./mole	$T_1$ , °K.	Cooling rate $-dT_1/dt$ , °K./μsec.	$-\left(\frac{1}{T_1^2}\right)\left(\frac{dT_1}{dt}\right)$ $\times 10^6$	Quenching rate: $\frac{d \log k}{dt}$
<i>cis</i> -Butene $\rightarrow$ <i>trans</i> -butene-2	65	1125	1.0	0.79	0.011
$C_4F_8 \rightarrow 2C_2F_4$	74.3	1120	1.0	.80	.013
$CH_3NC \rightarrow CH_3CN$	37	785	0.43	.69	.006

 TABLE II  
 EXPERIMENTAL DETAILS FOR THE ISOMERIZATION OF METHYL ISOCYANIDE<sup>a</sup>

Run	$p_1$ , mm.	$\frac{p_6}{p_1} p_1(\text{Ar})$	$\frac{p_6}{p_1} p_1(\text{CH}_3\text{NC})$	$T_1$ , °K.	Cor. $T_1$ (°K.) = $T_1 + (\Delta T/2)$	Effect. dwell time, μsec.	Extent of reacn.	$k$ , sec. <sup>-1</sup>
1	195	688	14.2	784	786	825	0.0804	101
2	180	623	12.9	773	776	902	.1103	128
3	175	588	12.1	752	754	770	.0732	167
4	166	628	12.9	832	842	770	.351	555
5	198	656	13.5	742	743	825	.0244	29.8
6	200.5	643	13.3	722	723	770	.0252	32.9
7	190	616	12.7	727	728	880	.0166	19.2
8	173	605	13.4	773	780	880	.2309	296
9	169	581	12.9	768	770	715	.0747	104
10	152	527	11.7	773	776	902	.1224	158
11	136	504	11.2	819	828	1100	.3104	332
12	122	462	10.3	832.5	847	1155	.5124	613
13	140	471	10.5	752	755	880	.145	139
14	143	501	11.1	819	827	968	.319	359
15	142	514	11.4	804	810	880	.237	267
16	173	571	12.7	742	744	880	.0744	49.7
17	172	566	12.6	739	741	924	.0762	49.3
18	169	551	12.3	732	734	880	.0578	29.5
19	120	457	10.2	845	857	1012	.426	511
20	167	523	11.5	708	708.5	1155	.0652	18.4
21	165	538	11.8	732	734	1012	.119	62.7
22	160	570	12.4	790	795	1012	.226	176
23	161	556	12.1	768	771	968	.134	80.9
24	160	573	12.5	790	797	1100	.276	211

<sup>a</sup> Runs 1-8 were made with 2.018% methyl isocyanide, runs 9-19 with 2.171%, and runs 20-24 with 2.140%.

used in these experiments. The values plotted must be compared with values extrapolated from low temperature range also taken at pressures in the fall-off region. For such a comparison we must accept the reported value of  $n$ , the effective number of oscillators, and assume a collision efficiency for excitation by argon relative to that by methyl isocyanide. The equations used are those given by Volpe and Johnston.<sup>6</sup>

$$\frac{f(\text{argon})}{f(\text{CH}_3\text{NC})} = \frac{b(\text{argon})}{b(\text{CH}_3\text{NC})} \left[ \frac{\sigma(\text{argon}) + \sigma(\text{CH}_3\text{NC})}{\sigma(\text{CH}_3\text{NC}) + \sigma(\text{CH}_3\text{NC})} \right]^{-2} \quad (3)$$

where  $b(\text{argon})/b(\text{CH}_3\text{NC})$  is the measured relative efficiency at a selected pressure,  $\{[\sigma(\text{argon}) + \sigma(\text{CH}_3\text{NC})]/2\sigma(\text{CH}_3\text{NC})\}^2$  is the collision diameter ratio, and  $f(\text{argon})/f(\text{CH}_3\text{NC})$  is the corresponding collision efficiency. Collision diameters of  $\sigma(\text{CH}_3\text{NC}) = 4.5 \text{ \AA.}$  and  $\sigma(\text{Ar}) = 3.42 \text{ \AA.}$ <sup>7</sup> were used. The corrected value for  $n = 5.5$  at 230° is given in footnote 13 of ref. 2. This was increased by 1.5 to allow for the fact that the shock temperatures were in the range of 500° (estimated on the basis of the theoretical values given in Table IX of ref. 1); thus  $n = 7.0$ . For a typical run the total reflected shock pressure at 770°K. was 1355 mm., of which 27.1 mm. was contributed by the methyl isocyanide. Using a collision diameter ratio of 0.774 and a relative efficiency of 0.05, we estimated that the total equivalent

methyl isocyanide pressure at this temperature would have been 78.5 mm. By means of Slater's equation, we then estimated that the corresponding low tempera-

$$\log p_6/p_1 = n/2 \log T_6/T_1 \quad (4)$$

ture pressure was 17.7 mm., for which the original investigators gave  $\log k/k^\infty = -0.498$ . The corresponding curve extrapolated to the high temperature region is that indicated in Fig. 1 by the dashed lines. The agreement between the extrapolated and observed data are well within the experimental error of the temperatures computed for the reflected shocks.

To justify the assumed value (0.05) for the relative collision efficiencies of argon and methyl isocyanide, data for seven unimolecular reactions were assembled for comparison in Table III. The reaction which appears to be most similar to the isomerization of  $\text{CH}_3\text{NC}$  is the one for *cis*-butene-2. Since Schneider and Rabinovitch found the relative efficiency of nitrogen to be 0.25, a value of approximately 0.05 is reasonable for argon. Had a higher relative collision efficiency been assumed, the discrepancy between the extrapolated and the median of the observed values would have been larger than indicated. It is evident from our observations that when the precision of shock tube data is greatly increased it will be possible to measure quite readily the relative collision efficiencies

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TABLE III  
RELATIVE INERT GAS EFFICIENCIES FOR SOME UNIMOLECULAR REACTIONS

Inert gas	Reacting molecule						
	CH <sub>3</sub> NC	Cyclopropane <sup>c</sup>	Cyclobutane <sup>c</sup>	N <sub>2</sub> O <sub>8</sub> <sup>c</sup>	N <sub>2</sub> O <sup>c</sup>	NO <sub>2</sub> Cl <sup>e</sup>	<i>cis</i> -butene-2 <sup>f</sup>
Ar	[0.05 <sup>a</sup> ]	0.07	0.21	0.15	0.20	0.21	0.08
N <sub>2</sub>	.25 <sup>b</sup>	0.07	0.21	0.23	0.24	0.29	0.32
C <sub>2</sub> H <sub>6</sub>	.6 <sup>b</sup>	..	..	..	..	..	..
Methane	...	0.24	0.38	..	..	..	..
Propylene	...	~1.0 <sup>d</sup>	..	..	..	..	..

<sup>a</sup> Assumed in this paper. <sup>b</sup> Ref. 1. <sup>c</sup> A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955, p. 84. <sup>d</sup> H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A217**, 563 (1953). <sup>e</sup> Ref. 6 in this paper. <sup>f</sup> R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **57**, 2226 (1961).

in the fall-off region for the excitation of molecular vibrations, in the high temperature regime.

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debted to Professor B. S. Rabinovitch for supplying details of the methyl isocyanide synthesis, and to Dr. Chava Lifshitz for help with the Fortran programs. H. F. C. wishes to thank the National Science Foundation for a Cooperative Fellowship during part of this work.

[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, THE DOW CHEMICAL CO., MIDLAND, MICH.]

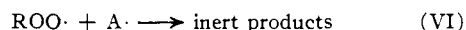
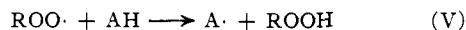
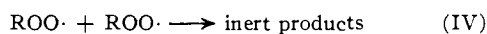
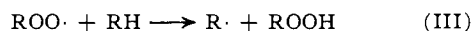
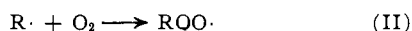
## Antioxidant Inhibition by Phenol<sup>1a</sup>

BY W. G. LLOYD<sup>1b</sup> AND C. E. LANGE

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The kinetics of oxidation retardation by the weak antioxidant phenol has been examined for two systems. Under nonbranching conditions retarded rates are proportional to the square root of initiator concentration and to the inverse square root of phenol concentration, as previously found by Hammond, Boozer, *et al.* The dependence of retarded rate upon substrate concentration in both nonbranching and branching systems is inconsistent with the complex termination mechanism. A hypothesis of "selective inhibition" is proposed.

Inhibition by phenolic antioxidants has been accounted for in terms of a straightforward transfer of the phenolic hydrogen atom to the chain carrier peroxy radical, thus forming a resonance-stabilized aryloxy radical which is incapable of continuing the kinetic chain.<sup>2,3</sup> Thus from the reaction scheme



where IN, RH, and AH denote initiator, substrate, and antioxidant, respectively, the retarded rate (assuming that reaction IV may be ignored)<sup>4</sup> is

$$-d(\text{O}_2)/dt = 2nk_1(\text{IN}) + (nk_1k_3(\text{IN})(\text{RH})/2k_5(\text{AH})) \quad (1)$$

This interpretation has been fruitful, *e.g.*, in deriving initiation rates from the observed retardation of weakly inhibited systems.<sup>5</sup> Several recent kinetic studies of autoxidation inhibition<sup>6</sup> and of polymerization inhi-

bition with<sup>7,8</sup> and without<sup>9</sup> oxygen present have been interpreted in terms of this simple radical transfer termination process. This view is further supported by evidence that antioxidant efficacy of substituted phenols may be correlated with Hammett  $\sigma$ -values,<sup>10</sup> phenolic O-H stretching frequencies,<sup>11</sup> the calculated stabilities of phenol-alkylperoxy radical "frontal" charge-transfer complexes,<sup>12</sup> ease of phenolic H-abstraction by diphenylpicrylhydrazyl radicals,<sup>13</sup> oxidation potentials,<sup>2,3,14,15</sup> and electrophilic substituent values.<sup>15</sup>

Clear indication of a greater kinetic complexity was afforded in the demonstration by Hammond, Boozer, and co-workers<sup>10</sup> that for such systems as tetralin in chlorobenzene at 62.5° with 2,2'-azobis(isobutyronitrile) (ABIN) and with a weak antioxidant such as phenol, retarded rates were proportional to the square root of initiator concentration and to the inverse square root of retarder concentration. These "anomalous" dependencies led to the proposal of a two-step termination mechanism, consisting of the fast, reversible formation of a complex between antioxidant molecule and peroxy radical followed by a slower, irreversible

(1) (a) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963. (b) Present address: The Lumms Co., Newark 14, N. J.

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