In like manner, other hydrazides were prepared, and melting points and yields are summarized in Table II.

2. 1,2-Propylene Diisocyanate.—A 2-1. beaker equipped with a thermometer and a mechanical stirrer and externally cooled in an ice bath was charged with 600 g. of ice, 100 ml. of carbon tetrachloride, 70 ml. of concentrated hydrochloric acid, and 57 g. (0.36 mole) of 2-methylsuccinic dihydrazide. A solution of 50 g. (0.73 mole) of sodium nitrite in 100 ml. of water pre-cooled to 0° was added dropwise to the stirred mixture over a period of 20 min. The temperature of the reaction mixture was maintained below 8° by addition of pieces of ice, and stirring was continued for 0.5 hr. after completion of the addition. The layers were separated, and the azide solution combined with two benzene extractions of the aqueous layer. The final volume⁸ amounted to about 400 ml. The solution was dried overnight over anhydrous calcium chloride and then refluxed for 4 hr. to complete decomposition of the azide. The refluxing solution developed a blue color which disappeared when the decomposition was essentially complete. Solvent was removed and the diisocyanate was then distilled at reduced pressure. After a short forerun, 19.6 g. (42%) of pure 1,2-propylene diisocyanate was collected as a lachrymatory liquid which had b.p. 83.5° (25 mm.) and n^{26} 1.4398.

Treatment with aniline gave a bis-phenylurea, m.p. 238-240°.

(8) It is essential that the solution be dilute at this stage, so that the heat generated by the slowly decomposing azide may be safely dissipated. More concentrated solutions retain sufficient heat to cause sudden and violent decomposition of the remaining azide.

Anal. Calcd. for $C_{17}H_{20}N_4O_2;\;$ C, 65.36; H, 6.45; N, 17.94. Found: C, 65.41; H, 6.45; N, 17.65.

Table III summarizes the properties and yields of the other isocyanates prepared in this work. All the isocyanates were extremely moisture-sensitive, so no elemental analyses were performed on the monomers themselves. Several monomers were derivatized with aniline, and the bis-phenylureas serve well to identify the isocyanates. 1,2-Propylene diisocyanate, 1,2cyclohexylene diisocyanate, and glyceryl triisocyanate apparently have not been prepared previously.

III. Infrared Analysis of Phenyl Isocyanate Dimer (1,3-Diphenyluretidinedione).—Although dimers of aromatic isocyanates (uretidinediones) have been known for many years,⁹ the carbonyl absorption of the four-membered heterocycle has not apparently been reported in the literature. The infrared absorption spectrum determined on a chloroform solution of phenyl isocyanate dimer, m.p. 177–178° (lit.¹⁰ 175–176°), showed a single sharp band at 5.60 μ due to carbonyl.

Acknowledgments.—The author is indebted to Dr. R. Zbinden and Miss Mary Schick for interpretation of the infrared spectra, and to Mrs. Raila M. Mason for determination of molecular weight by osmometry.

(9) J. H. Saunders and R. J. Slocombe, Chem. Rev., 43, 211 (1948).
(10) J. S. Blair and G. E. P. Smith, Jr., J. Am. Chem. Soc., 56, 909 (1934). We are indebted to Dr. K. C. Smeltz for a sample of pure phenyl isocyanate dimer.

[Contribution from the Department of Chemistry, Purdue University, Lafayette, Ind.]

Displacement Reactions. V. The Reaction of Cyanide Ion with Tetramethylthiuram Disulfide¹

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The reaction of tetramethylthiuram disulfide with cyanide ion has been found to be a two-step process in which the dimethyldithiocarbamate intermediate rises to concentrations allowing spectral analysis or isolation. The two SN2 displacement reactions are discussed in terms of the oxibase scale relating oxidation electrode potential and basicity of the nucleophile to its reactivity. An estimate of 2.12 ± 0.04 Å, is given to the S-S bond length in the disulfide by the correlation of activation energy with bond distance.

Introduction

The displacement reactions on a divalent sulfur atom divide into three stoichiometric classes.^{4,5}

$$\begin{array}{ccc} X - Y & + SZ & (a) \\ X - S - Y + Z - \vdots & XS & + YZ & (b) \end{array}$$

$$\frac{1}{X-S-Z+Y} \qquad (b)$$

Numerous examples of kinetic and mechanistic studies have been reported for type c reactions.^{4–6} While the reaction of cyanide ion with tetramethylthiuram disulfide has the same stoichiometry⁷ as the type a,

$$\begin{array}{cccc} CH_3 & S & S & CH_3 \\ & & & \\ & & & \\ CH_3 & & CH_3 \end{array} + -CN \longrightarrow \\ CH_3 & & CH_3 & S & CH_3 \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\$$

it is unlikely from the work of Cambron⁸ that reaction 1 represents the *mechanism* as well as the over-all reaction. Indeed Cambron's work and suggested

(1) Paper IV: R. E. Davis, A. Cohen, and J. Louis, J. Am. Chem. Soc., 85, 3050 (1963).

(2) Alfred P. Sloan Fellow, 1962-1964.

(3) Taken in part from the M.Sc. thesis, January, 1963.

(4) R. E. Davis, Vol. 11, Chapter 1, of "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press, New York, N. Y., in press.

- (5) R. E. Davis, Vol. II in "Survey of Progress in Chemistry," A. Scott, Ed., Academic Press, Inc., New York, N. Y., in press.
- (6) Reviewed also in W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(7) J. Von Braun and F. Stechele, Ber., 36, 2275 (1903).

(8) A. Cambron, Can. J. Research, 2, 341 (1930).

mechanism have been found to be correct in the present study. In continuation of a series of studies on the SN2 reaction at divalent sulfur atoms, we wish to present a detailed kinetic and mechanistic investigation of this reaction of an excellent thiophilic⁹ reagent, cyanide ion, with a compound containing a thiuram disulfide sulfursulfur bond.

Results

Ultraviolet Spectra.—The ultraviolet spectrum of the nearly colorless tetramethylthiuram disulfide (TMTD) is characterized by strong absorption increasing below 300 m μ with a plateau between 280 and 240 m μ and finally increasing toward 200 m μ .¹⁰ The monosulfide (TMTM) is yellow and has one strong maximum near 275 m μ in methanol and a minimum near 240 m μ .¹⁰ In Fig. 1 the spectrum of a mixture of TMTD and TMTM each at 5 × 10⁻⁵ M in methanol is reproduced. Also in this figure is the spectrum of a solution containing initially 10 × 10^{-5} M in TMTD and some cyanide ion after 50% reaction. From this figure one concludes, in accord with Cambron's results, that the reaction is not a onestep process but that intermediates are present in measurable concentrations. Also presented in Fig. 1 is the spectrum of the dimethyldithiocarbamate with its characteristic double camel hump near 285 and 250 m μ .

Isolation of an Intermediate.—Cambron⁸ suggested and demonstrated that a dithiocarbamate could react with a thiocarbamyl thiocyanate to produce a thiuram monosulfide and thiocyanate ion. It seemed most reasonably to suggest that reaction 1 has a two-step

(9) P. D. Bartlett and R. E. Davis, J. Am. Chem. Soc., 80, 2513 (1958).

(10) R. E. Davis and C. Perrin, ibid., 82, 1590 (1960)

TMTD $M \times 10^5$	KCN , $M \times 10^4$	Solution	Salt $M \times 10^3$	T °C	k_1, M^{-1}	k_2, M^{-1}
4 46	12.6	MeOH		25.0	1.5	
3 20	7.5	MeOH	a	25.0	1.5	
3.03	15.3	MeOH-H ₂ O ⁴	50% phosphate ^b	25.0	0.7	
1.00	2.50	MeOH		21.6	1.3	0.7
1.02	5.60	MeOH		21.6	1.2	0.7
2.0	43.6	MeOH		21.6	1.2	
9.98	5.60	MeOH ^c		21.6	1.1	0.6
12.1	10.9	MeOH		21.6	1.2	0.4
2.02	10.0	MeOH	KSCN 6.00	21.6	1.1	
2.02	10.9	MeOH	KSCN 1.20	21.6	1.3	
2.02	10.9	MeOH	KCl 2.50	21.6	1.2	
2.02	10.9	MeOH	KCl 5.0	21.6	1.1	
2.02	10.9	MeOH	KCl 12.0	21.6	1.0	
4.37	5.97	MeOH		15.0	0.83	
4.57	6.54	$MeOH-H_2O^a$	$10\%^{a}$	15.0	. 80	
4.95	7.38	MeOH-H ₂ O	40%	15.0	. 72	
1.01	5.75	$MeOH-H_2O$	70%	15.0	. 70	
2.02	1.09	MeOH		11.4	. 60	
2.03	1.08	MeOH		11.4	. 63	
2.05	10.0	$MeOH^{c}$		5.0	.47	0.14
2.53	9.80	MeOH-H ₂ O	70%	5.0	. 36	
2.40	10.7	MeOH-H ₂ O	10%	5.0	. 43	
10.0	1.30	$MeOH-H_2O^c$	10%	5.0	.40	0.10

TABLE I REACTION OF TETRAMETHYLTHIURAM DISULFIDE WITH POTASSIUM CYANIDE

^a Volume %. ^b pH 5.6. ^c A small amount of sodium methoxide was added to suppress the hydrolysis of the cyanide and to prevent the decomposition of the dithiocarbamate.

$$(CH_{s})_{2}NCS^{-} + (CH_{3})_{2}NC^{-}SCN \xrightarrow{R_{2}} TMTM + -SCN \quad (3)$$

mechanism. An attempt to isolate the thiocarbamyl thiocyanate was made by mixing TMTD and potassium cyanide in methanol followed by the addition of hydrochloric acid in a good hood to destroy the dithiocarbamate¹¹ and remove cyanide ion. An unstable impure fraction was obtained that had an infrared band near 4.5 μ which might be the stretching frequency of the carbon-nitrogen triple bond in II. However, the zinc salt of the dithiocarbamate was isolated in the reaction of zinc cyanide with TMTD. In this case the zinc salt was obtained in high yield. Another unstable, impure fraction was obtained that might have been II. It produced thiocyanate ion upon standing in numerous solvents. Thus there is good evidence both spectroscopic and chemical for the two-step processes 2 and 3.

Kinetics.—A detailed analysis of the time behavior of TMTD and cyanide supports the two-step mechanism 2 and 3. Some experiments were run with equivalent concentrations and the data fitted with the equations of the appendix. It was more convenient to run the reaction with a large excess of cyanide. The data are presented in Table I. All kinetic data were processed on a computer. See Fig. 2 for a typical experiment.

The reaction is first order in TMTD over a 12-fold variation in initial concentration and nearly first order in cyanide ion. Control of cyanide ion with low pH means that the dithiocarbamate will decompose.

The rate constant k_1 is depressed by the addition of inert salts and by dilution of the methanol with



Fig. 1.—Ultraviolet spectra in methanol of TMTD, the synthetic mixture of one part TMTD and one part TMTM, and the observed spectrum of TMTD + KCN at 50% reaction. Also included is the spectrum of dimethyldithiocarbamate. Concentrations are $5.0 \times 10^{-6} M$.

water. Both effects are consistent with the reaction of a charge ion with a neutral molecule with charge

$$(CH_{3})_{2}NCS_{2}^{-} + H^{+} \xrightarrow{k_{3}} (CH_{3})_{2}NH + CS_{2} \qquad (4)$$
$$(CH_{3})_{2}NH + H^{+} \xrightarrow{\text{fast}} (CH_{3})_{2}NH_{2}^{+}$$
$$rate = k_{3}[H^{+}][(CH_{3})_{2}NCS_{2}^{-}]$$

 $k_3 = 1.6 \times 10^{+2} M^{-1}$ sec. ⁻¹ at 25° in water (pH range 5.9 to 8.4)

^{(11) (}a) G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Press, New York, N. Y., 1962; (b) M. Hallaway, *Biochim. Biophys. Acta*, **36**, 538 (1959); (c) P. Zuman and R. Zahradnik, Z. physik. Chem., **208**, 135 (1957); (d) R. Zahradnik and P. Zuman, Chem. Listy, **52**, 231 (1958).



Fig. 2.—Optical density vs. time at 248 m μ for a solution of 4.46 \times 10⁻⁵ M TMTD and 1.26 \times 10⁻³ M KCN in methanol at 25°.

being dispersed in the activated complex. The activation energy for the reaction is low, being about 10 kcal./mole, a value typical for the reaction of cyanide ion with labile sulfur-sulfur bonds.⁴⁻⁶

Discussion

Thiophiles and Displacement Reactions.—Cyanide ion is easily oxidized and quite basic, therefore it is a very good nucleophile for a displacement reaction on a sulfur-sulfur bond.^{4,5,12} Expressed in the quantitative terms of the oxibase scale.^{4,5} E = 2.79 and H = 10.88. Yet cyanide ion will readily displace another very good nucleophilic material, the dithiocarbamate.¹³ Using the data of Ogston on the displacement of diethyldithiocarbamate on the mustard cation, the value of E = 2.39 and H = 5.74 can be calculated.⁵ These values will be good estimates for the dimethyl derivative.

Thus in terms of the oxibase scale and the E- and H-values of the nucleophile and the leganion,¹⁴ both the E decreases and the H decreases. Both of these

(12) The use of oxidation potentials of $2X^- \rightarrow X_2 + 2e^-$ to correlate relative displacement orders was first made by O. Foss (Acta Chem. Scand., 1, 307 (1947); in "Organic Sulfur Compounds," N. Kharasch, Ed., Vol. I, 1961, pp. 75-96). Edwards (J. O. Edwards, J. Am. Chem. Soc., 76, 1540 (1954); 78, 1819 (1956); J. O. Edwards and R. G. Pearson, *ibid.*, 84, 16 (1962)) then suggested his empirical *double basicity* scale combining both the oxidation potential and the basicity. We call the scale the oxibase scale.

A theoretical justification using nonequilibrium thermodynamics has been made.^{4,3} We would rather use the electrode potentials than the polarizability term of Edwards.

The linear-free energy relation is

$$\log \left(k_{\rm x}/k_{\rm H_{2}O} \right) = \alpha E + \beta H$$

hrr o

where k_x is the second-order rate constant of

$$X^- + A - Y \xrightarrow{R_X} XA + Y^-$$

and kH2O refers to

$$H_2O + A-Y \xrightarrow{\kappa_{H_2O}} HOA + H^+ + Y^-$$

The *E*-value is the oxidative electrode potential relative to water and the *H* is the pK_a of X ⁻ plus the log of water concentration. Thus *H* is the pK_a of a single X ⁻ compared to a single water molecule.

$$X^- + H_3O^+ \longrightarrow HX + H_2O$$

The constants α and β are characteristic of the substrate A-Y. A novel interpretation^{4,5} has been made concerning α and β . The term α is a measure of the *ease of reduction* of A-Y and is proportional to the *E*-value of the leaving group. The term β is a measure of the acidity and the amount and degree of charge near the reaction center in A-Y.

(13) A. G. Ogston, E. R. Holiday, J. St. L. Philpot, and L. A. Stocken, Trans. Faraday Soc., 44, 45 (1948).

(14) A word suggested in ref. 4 and 5 for a leaving group anion, from leg_0 (Greek), to leave off. A neutral species would be a *legite*

changes result in a favorable free energy change and process is spontaneous.

$$CN^{-} \xrightarrow{\text{process } 2}{\Delta F < 0} (CH_3)_2 NCS_2^{-}$$
(5)

$$E \ 2.79 \longrightarrow 2.39 \text{ decrease}$$

$$H \ 10.88 \longrightarrow 5.74 \text{ decrease}$$

It is quite obvious from the use of the oxibase scale that cyanide *would not* add to the C=S bond and

displace the
$$(CH_3)_2NCSS^-$$
 anion. An estimate of

$$S$$

$$CN^- \xrightarrow{\text{process 7}} (CH_3)_2NCSS^- \qquad (6)$$

$$E = 2.79 \longrightarrow 2.9 \text{ increase}$$

$$H = 10.88 \longrightarrow 11 \text{ to } 13 \text{ increase}$$

the oxidative dimerization potential of this polysulfide^{4,5} ion would place E near 2.9. An estimate of the pK_a would place H between 11 and 13. Thus the E increases and the H probably increases. As most of the effect^{4,5} is in the change of E-values, this process 7 has an unfavorable ΔF and would not occur.

$$\Gamma MTD + CN - \frac{unfavorable}{\Delta F > 0} \xrightarrow{K} (CH_3)_2 NCCN + (CH_2)_2 NCSS^{-1}$$
(7)

The thiocarbamate will easily displace the thiocyanate leganion. In this case the changes of both E and H are quite favorable.

$$(CH_{3})_{2}NCS_{2} \xrightarrow{\text{process } 3} -SCN$$

$$E 2.39 \longrightarrow 1.83 \text{ decrease}$$

$$H 5.74 \longrightarrow 1 \text{ decrease}$$

The Energetics of the System.—In 1960, Davis,¹⁰ discussing the thermochromism properties of TMTD, reported the heat of reaction 1 in methanol using a

$$MTD + NaCN \longrightarrow TMTM + NaSCN \qquad (1)$$

 $\Delta H = -19.8 \pm 0.4 \text{ kcal./mole}$

Т

simple calorimeter. Using this datum and the heats of formation of sodium thiocyanate and sodium cyanide, an estimate¹⁰ was given for the ΔH of

$$TMTD \longrightarrow TMTM + \frac{1}{8} S_8$$
(8)
$$\Delta H = -2.4 \text{ kcal./mole}$$

Recently McCullough¹⁵ measured the heats of combustion and of formation of TMTD and TMTM using a precision rotating bomb calorimeter. Using their values of $\Delta H_{\rm f}^{\circ}$ (solid) of 11.44 ± 0.30 kcal./mole for TMTM and 9.74 ± 0.41 kcal./mole for TMTD, we have calculated the ΔH of (1) to be -17.20 ± 0.70 and the ΔH of (8) to be -1.70 ± 0.71 kcal./mole. The agreement of our data, simply obtained, with more exacting data is quite good. Some correction would be needed as the $\Delta H_{\rm f}^{\circ}$'s refer to the solids and our values refer to homogeneous solution in methanol.

An Estimate of the Sulfur–Sulfur Bond Length by Kinetic Methods.—The activation energy for the initial reaction 2 is low. Using the empirical correlation¹ between the activation energy and the sulfur–sulfur bond length, an estimate of 2.12 ± 0.04 Å. is placed on the sulfur–sulfur bond length in TMTD.¹⁶ Such a value is consistent with the general reactivity and thermal

(15) W. D. Good, J. L. Lacina, and J. P. McCullough. J. Phys. Chem., 65, 860 (1961).

(16) An X-ray analysis of TMTD has been suggested to Prof. Olav Foss, personal communication, spring, 1963.

instability of TMTD, $^{10, 17-20}$ and the resonance stability of the dithiocarbamyl free radical, R_2NCS_2 .

Experimental

Materials.—Eastman Kodak Yellow Label tetramethylthiuram disulfide was recrystallized.¹⁰ The monosulfide was isolated from the reaction of TMTD (Yellow Label, not purified) with potassium cyanide in methanol. The product was recrystallized from aqueous methanol, isolated in 88% yield (m.p. $105-106^\circ$, corrected). Methanol was refluxed over magnesium turning and distilled through an 8-ft. packed column. The fraction boiling at 64.5° (750 mm.) was stored in the dark. Potassium cyanide (Baker reagent) was standardized against silver nitrate. The cyanide solutions were prepared daily. Potassium chloride and thiocyanate (Baker reagents) were dried at 110° .

Kinetics.—A Cary Model 14 spectrometer or a thermostated Beckmen DU with 1-cm. cells were used. All kinetic data were treated on a Royal McBee RPC-4000 digital computer using a program written by A. C. An estimate of the standard deviation was also provided.

Isolation.—Zinc cyanide (0.10 mole) was suspended in 600 ml. of methanol. The solvent was then allowed to reflux slowly through the thimble of a Soxhlet extractor containing 0.10 mole of TMTD. After the TMTD had been added, the solution was partially concentrated. The white solid removed by filtration was washed with acetone. From the acetone solution 0.09 mole of the zinc dithiocarbamate was obtained, identical in all respects with a known sample in the infrared, n.m.r., ultraviolet, and melting point.

Further concentration of the original methanol solution resulted in an unstable oil having strong absorption near 4.5 μ . Numerous attempts failed to win a pure product.

Appendix

The differential equations for the kinetic system

$$A + B \xrightarrow{k_1} C + D$$
$$C + D \xrightarrow{k_2} E + F$$

have not been solved in closed form. If one uses equivalent concentrations, then A = B, C = D, E = F. In this case

$$2A \xrightarrow{k_1} 2C$$
 (i)

$$2C \xrightarrow{\sim} 2E$$
 (ii)

and solution is possible. The solution of system (i and ii) has not been reported in the literature. From i

$$A = \frac{A_0}{1 + A_0 k_1 t} = \frac{A_0}{\tau}$$
(iii)

Then

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k_1 \frac{(A_0)^2}{\tau} - k_2 C^2 \qquad (\mathrm{iv})$$

$$C = \frac{1}{k_2 u} \frac{\mathrm{d}u}{\mathrm{d}t}$$

and

Let

and

$$k_2/k_1 = k \qquad (vii)$$

Then iv becomes

$$\frac{\mathrm{d}^2 u}{\mathrm{d}s^2} - \frac{\mathrm{d}u}{\mathrm{d}s} - ku = 0 \qquad (\mathrm{viii})$$

Solution of viii using the differential operator D = d/ds gives

 $e^s = \tau$

$$u = g_1 \exp \left\{ \frac{1}{2} + \frac{1}{2} (\sqrt{1+4k})s \right\} + g_2 \exp \left\{ \frac{1}{2} - \frac{1}{2} (\sqrt{1+4k})s \right\}$$
(ix)

with g_1 and g_2 constants. Defining

$$\lambda = \sqrt{1+4k} \qquad (\mathbf{x})$$

and evaluation of g_1 and g_2 with the boundary conditions $\tau = 1$ and C = 0 at t = 0

$$C = \frac{A_0}{2\tau} k \left[\lambda + 1 - \frac{2\lambda}{1 + \left(\frac{\lambda - 1}{\lambda + 1}\right)\tau^{\lambda}} \right]$$
(xi)

Then as

$$dE = k_2 C^2 dt = k_1 A^2 dt - dC$$
$$E = A_0 \left[1 - \frac{1}{\tau} \right] - C$$
(xii)

The value of k_1 can best be obtained from expression iii obtained from a time study of the concentration of A. The value of k_2 can be estimated by plotting the concentrations of A, C, and E vs. τ^{-1} ; C reaches a maximum at $t_{\rm c}$ max when dC/dt and $d^2C/dt^2 = 0$.

An analytical expression then relates k_1 , t_{max} , and k_2 . These operations are quite rapid on a computer.

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 (\mathbf{v})

(vi)

⁽¹⁷⁾ J. C. D. Brand and J. R. Davidson, J. Chem. Soc., 15 (1956).

⁽¹⁸⁾ C. Walling, "Free Radicals in Solutions," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 335-341.
(19) T. E. Ferington and A, V. Tobolsky, J. Am. Chem. Soc., 77, 4510

^{(195);} **B**, 3215 (1958).

⁽²⁰⁾ D. Craig, Rubber Chem. Tech., 30, 1291 (1957).