hydrolysis of ethyl dichloroacetate in acetone–water mixtures. The present curves have a less negative slope in regions of lower dielectric constant instead of changing to a positive slope as was found by Nair and Amis.

FAYETTEVILLE, ARK.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Pyrolysis of Lead Oxalate; Isotope Effects and Product Composition

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The composition and isotopic constitution of the gaseous products of the pyrolysis of lead oxalate have been studied for reaction between 350 and 625°. Variations with temperature of the ratio of carbon dioxide to carbon monoxide in the product gases and of carbon isotope distribution are considered in terms of simple models in which: (a) it is assumed that the primary products are modified by a secondary reaction among themselves which competes with escape of the gaseous products from the decomposing mass, or (b) oxygen abstraction and C–C bond rupturing processes are presumed to compete. Models in group (a) are shown to correspond to temperature dependences of the molar yield ratio of gaseous products which are not in accord with observation. Consideration of models in group (b) is based primarily on the Bigeleisen–Wolfsberg treatment of three center reactions; satisfactory agreement with experiment is obtained for a model of the activated complex which includes a lead atom.

Introduction

Several investigations have been made of the products obtained when crystalline lead oxalate is decomposed thermally. At temperatures of pyrolysis above about 250° all of the carbon can be obtained as carbon dioxide or monoxide, but there is little unanimity concerning the molar ratio, Y, of these gases in the products. Maumene[1] finds $Y = 2$ and records the stoichiometry $3PbC_2O_4 = 2PbO + Pb + 4CO_2 + 2CO$, while mentioning that previous workers observed Y to be 3. Maumene reported that at higher temperatures some reduction of lead oxide to metal may occur; Sveda[2] studied the pyrolysis in an initially evacuated vessel and found that the extent of this reduction was proportional to the time of contact between solid and gaseous products of the primary reaction.

Denham[3] found that there was no reaction between the solid product (which he and Pascal and Minne[4] believed to be a lead suboxide) and the carbon monoxide produced if the total pressure was below 5 cm. at 270°; he reported $Y = 3$.

Bircumshaw and Harris[5] studied the products of the decomposition at temperatures in the range 310–470°. They found a dioxide/monoxide ratio of 2, established by X-ray and electrical conductivity measurements that the solid was a mixture of metallic lead and red tetragonal lead oxide, and observed that removal of the gaseous products by continuous pumping had only a slight effect on their composition. In a second paper[6] the kinetics of the pyrolysis was studied at temperatures between 309 and 350°. The rate data conformed to predictions based on a model in which decomposition starts at nuclei and spreads through branching chains along paths of lateral strain; the strain is relieved by the formation of Smekal cracks along which the decomposition is favored.

In the present paper we report a study of the composition and isotopic constitution of the gaseous products over the temperature range 350–625°. The study was carried out to elucidate the character of the molecular mechanism of the process, and no kinetics measurements were made.

Experimental

Lead Oxalate.—A slight excess of aqueous reagent oxalic acid was added slowly with constant stirring to a 1 *M* aqueous solution of reagent grade lead nitrate; after standing in contact with the supernatant for one hour at room temperature, the lead oxalate was removed by filtration, washed with distilled water, then dried in air for 3 hours at 110°.

Apparatus and Procedure.—The pyrolyses were carried out in a stream of dry, oxygen-free helium. The train employed was made up as follows. Sample decomposition took place in a 2 cm. i.d. Vycor tube, the second half of which passed through an electric furnace which maintained a predetermined temperature constant to 2°; the gaseous products passed first through a trap cooled in liquid nitrogen, thence to a combustion tube at 750° filled with copper oxide wire, and finally through another trap cooled in liquid nitrogen. Preliminary tests showed that carbon monoxide and carbon dioxide were separated quantitatively in the first trap at the helium flow rate employed (50 cc. per min.). In a typical experiment 0.45–0.50 g. of lead oxalate was weighed into a shallow platinum boat which was placed in the unheated end of the pyrolysis tube. The train was assembled and the helium flow maintained for one hour to remove traces of oxygen. At the start of most of the runs the pyrolysis tube was tipped, causing the boat to slide into the heated zone. Since the reaction becomes very rapid at the higher temperatures employed, a few runs in that region were made in which the contents of the boat were dumped by an externally operated tipper onto a thick platinum foil in the heated zone to ensure the most rapid possible heating to the run temperature. At 350° the decomposition is complete in 40 minutes[6]; so that no time variable would be introduced, the helium sweep was maintained for 60 minutes in all runs. The two gaseous samples were measured manometrically, then reserved for mass spectrometric analysis.

Isotope Analyses.—The procedures and calculation methods used for the carbon isotope ratio determinations have been detailed in previous publications from this Laboratory.[7,8] The final oxygen isotope ratios were obtained by applying to the observed values of the ratio $(m/q\ 46)/m/q\ 44 + 45)$ corrections for the magnitude of $(m/q\ 45)/(m/q\ 44)$, and for daily variations in the response of the mass spectrometer; analysis showed that corrections to these ratios for incomplete resolution and the contribution to the peak at m/q 46 of the species $C^{13}O^{16}O^{17}$ (assumed

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(1) E. J. Maumene, *Bull. soc. chim.*, **13**, 194 (1870).

(2) J. Sveda, *Chem. Listy*, **17**, 47, 81, 112 (1923).

(3) H. G. Denham, *J. Chem. Soc.*, 29 (1917).

(4) P. Pascal and P. Minne, *Compt. rend.*, **193**, 1303 (1931).

(5) L. L. Bircumshaw and I. Harris, *J. Chem. Soc.*, 1637 (1939).

(6) L. L. Bircumshaw and I. Harris, *ibid.*, 1898 (1948).

(7) P. E. Yankwich and R. L. Belford, THIS JOURNAL, **75**, 4178 (1953).

(8) P. E. Yankwich and R. L. Belford, *ibid.*, **76**, 3067 (1954).

constant) were so small that considerable uncertainty in them produced no variation in the final corrected ratio.

Results

The corrected carbon and oxygen isotope ratios of the samples of carbon dioxide and carbon monoxide (measured in the form of the dioxide) products are given in Table I. In Table II are collected the calculated values of the ratios $R_r = (R^c_{CO_2}/R^c_{CO})$ and Y = (moles CO_2 product/moles CO product) for each run. The average values of Y and R_r are plotted against each other in Fig. 1; the horizontal and vertical bars represent the errors given in Table II.

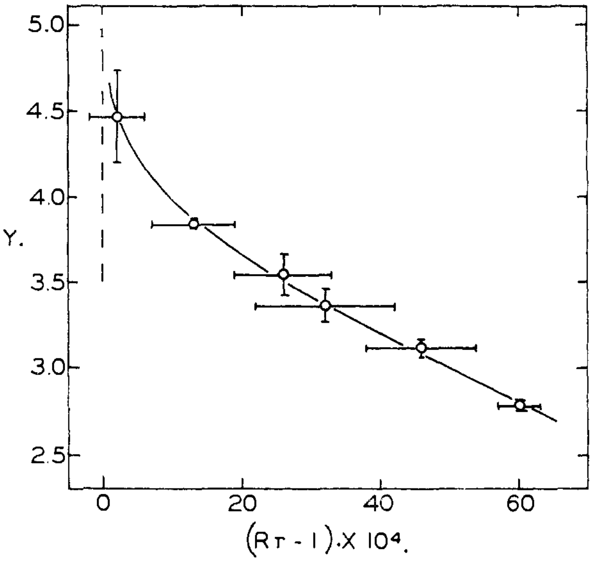

Fig. 1.—Molar ratio CO_2/CO, Y, *vs.* ratio of carbon isotope ratios, R_r.

TABLE I

CORRECTED CARBON (C^{13}/C^{12}) AND OXYGEN (O^{18}/O^{16}) ISOTOPE RATIOS OF CARBON DIOXIDE AND CARBON MONOXIDE PRODUCT GASES

(All R values have been multiplied by 10^6)

Temp., °C.	Run	$R^c_{CO_2}$	R^c_{CO}	$R^0_{CO_2}$	R^0_{CO}
350	7	10846[9]	10779	4257[9]	4208
	8	10848	10784	4258	4208
400	10	10864	10796	4256	4197
	11	10842	10800	4250	4193
	12	10841	10798	4255	4203
	13	10821	10775	4246	4202
450	14	10828	10805	4250	4196
	15	10833	10790	4244	4201
	16	10848	10807	4254	4201
	17	10842	10797	4253	4202
	31	10830	10810	4252	4204
500	18	10832	10803	4249	4202
	19	10835	10800	4253	4206
	20	10841	10809	4251	4201
	32	10837	10822	4251	4202
550	21	10827	10821	4244	4194
	22	10837	10814	4247	4200
	23	10835	10822	4248	4199
625	24	10828	10828	4249	4198
		10832	10828	4246	4198
Tank CO_2		10789		4180	

TABLE II

VALUES OF THE RATIOS $R^c_r = (R^c_{CO_2}/R^c_{CO})$ AND Y = (MOLES CO_2/MOLES CO) FOR THE GASEOUS PRODUCTS

Temp., °C.		R_r	Y
350		1.0062	2.79
		1.0059	2.75
	Av.	1.0060 ± 0.0003[10]	2.77 ± 0.02[11]
400		1.0063	3.06
		1.0039	3.14
		1.0040	3.07
		1.0043	3.16
	Av.	1.0046 ± 0.0008	3.11 ± 0.04
450		1.0021	3.52
		1.0040	3.31
		1.0038	3.32
		1.0042	3.19
		1.0019	3.44
	Av.	1.0032 ± 0.0010	3.36 ± 0.10
500		1.0027	3.43
		1.0032	3.41
		1.0030	3.60
		1.0014	3.73
	Av.	1.0026 ± 0.0007	3.54 ± 0.12
550		1.0006	3.80
		1.0021	3.87
		1.0012	3.81
	Av.	1.0013 ± 0.0006	3.83 ± 0.03
625		1.0000	4.73
		1.0004	4.19
	Av.	1.0002 ± 0.0004	4.46 ± 0.27

At the helium flow rate of 50 cc. per min. the mean contact time of product gases with the decomposing sample is about 8 seconds; the residence time of the burning carbon monoxide in the combustion tube is 60–65 seconds. Titani, Nakata and Kanome[12] observed the exchange of O^{18} between carbon dioxide and cupric oxide after a contact time of 75 seconds to be 15% complete at 430° and 48% complete at 530°.[13] It is probable then that the carbon dioxide obtained from combustion of the product carbon monoxide is in exchange equilibrium with the copper oxide with respect to O^{18}; if this situation obtains, the differences between R^0_{CO} and the value of $R^0_{CO_2}$ for tank carbon dioxide should be constant. Examination of the data in Table I shows this conclusion to be valid, except for the runs at 350°.

While the oxygen isotope ratio data for carbon monoxide product furnish no useful information about the pyrolysis, those for carbon dioxide may if there is no appreciable exchange between dioxide and monoxide in the pyrolysis tube. The carbon dioxide–carbon monoxide exchange is extremely slow at 800° in quartz vessels[14]; any exchange under the conditions of our experiments presumably would be catalyzed by the decomposing solid.

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[9] The uncertainty in a ratio is ±2 or less in the last digit.

[10] Includes the uncertainty in the isotope ratios.

[11] Average deviation from the mean.

[12] T. Titani, S. Nakata and A. Kanome, *Bull. Chem. Soc. Japan*, **17**, 288 (1942).

[13] Exchange of about 40% was observed at 580 and 630°, but their analytical method was not of high precision. For our purpose, the important fact is that the exchange is reasonably rapid at temperatures above 400°.

[14] T. H. Norris and S. Ruben, *J. Chem. Phys.*, **18**, 1595 (1950); T. Hayakawa, *Bull. Chem. Soc. Japan*, **26**, 165 (1953).

This point can be tested by comparing the observed values of R_r as a function of temperature with those calculated for exchange equilibrium from the data of Urey[15]; since the mechanism of the exchange involves oxygen atom transfer, carbon and oxygen isotope exchanges must occur simultaneously.[16] It is observed that, at all temperatures, the value of R_r is much smaller than that calculated for complete exchange (at 350°: obsd. 1.0060, calcd. 1.0275; at 625°: obsd. 1.0002, calcd. 1.0160); further, if the exchange were very rapid at the higher temperatures employed, one would expect a plot of ln R_r *versus* $1/T$ to exhibit a positive second derivative since the value of R_r must approach from below that calculated for complete exchange. We conclude that exchange of carbon and oxygen between carbon dioxide and carbon monoxide products is inappreciable under the conditions of the pyrolysis.

Discussion

Variation of Y with Temperature.—While it has been found that the proportions of the product gases are altered if the pressure in the system is maintained at a low value by pumping, the data of Bircumshaw and Harris[5] indicate that the effect is small compared with the variations observed in this research. The kinetics study of the same workers[6] shows that the reaction does not take place in the bulk of the crystals, but in cracks on the surfaces and at imperfections. Consider two situations in which the primary products are modified by a secondary *reaction* among themselves, which competes with *escape* of the gaseous products from the decomposing mass: case I—lead and carbon dioxide primary products, subsequent partial reduction of the carbon dioxide to the monoxide; case II—a simple oxygen abstraction primary process yielding equimolar amounts of lead oxide and the two carbon oxides, subsequent partial oxidation of carbon monoxide to the dioxide. Ignoring the isotope effect, assume that both the *reaction* and *escape* processes may be considered pseudo-first order with respect to carbon; then define the appropriate rate constants as k_r and k_e, respectively, and let $(k_e/k_r) = (1 - \alpha)/\alpha$. For case I, $Y = (1 - \alpha)/\alpha$; for case II, $Y = (1 + \alpha)/(1 - \alpha)$. It seems likely that the activation energy of the forward or reverse of the reaction $Pb(s) + CO_2(g) = PbO(s) + CO(g)$ is of the order of 40–50 kcal. per mole. The escape process may be similar to any of these: simple unactivated diffusion through the interstices of the decomposing powder mass, activated surface diffusion, desorption from an original chemisorbed state, or diffusion through the bulk of individual crystallites from a depth of at least a few tens of ion layers; the maximum apparent activation energy associated with any of these is of the order of 15–20 kcal. per mole, which would require that α increase rapidly with increasing temperature. For case I, Y would decrease with increasing temperature; for case II, Y would increase very rapidly with temperature. Neither situation corresponds to that observed, so we reject those models which require competition between escape and secondary reaction.

It is possible that the mechanism of the decomposition involves an intra-ionic competition between two processes, one which results in conversion of an oxalate ion into two molecules of carbon dioxide and another, with a somewhat lower activation energy, which results in the formation of one molecule each of carbon monoxide and dioxide. In suggesting such a model we presume that no chemical process occurs during the diffusion of the product gases out of the solid mass. If the intra-ionic reactions are assumed to be first order, and the specific rate constants are k and k', respectively, then $Y = (2k + 4k')/(4k')$ and the activation energy difference obtained from the observed temperature dependence of Y is 2.7 ± 0.1 kcal. If the required electron transfer from oxalate ion to lead takes place before gross bond ruptures within the ion, this activation energy difference can be related to the C–C bond energy in the first reaction and the energy of the C–O bond, or of motion of O in a triad such as C–O–Pb, in the second. In the absence of more information we conclude only that the second reaction probably involves something more complex than rupture of a simple C–O linkage since the activation energy difference in that case would be more than a few kcal. per mole.

Calculation of Isotope Effects through Two-center and Three-center Models.—Methods for the calculation of the ratios of isotopic rate constants have been developed by Bigeleisen[17] extending the work of Bigeleisen and Mayer.[18] The usual application, which has been successful in a number of cases,[19] involves the assumption of a two-center model, the effective masses of the activated molecules along the coördinate of decomposition in the transition state being calculated by the method of Slater.[20] As a refinement, Bigeleisen and Wolfsberg[21,22] derived these effective mass ratios, μ, for the three-center system A–B–C, in which a bond between atoms B and C is broken and a bond between atoms A and B is formed. The final corrected formula for these temperature independent factors[22] involves a term whose coefficient is (−cos ABC), and depends on atomic masses and a parameter p which, for this situation, is the square of (amount of bond formation between A and B)/(amount of bond extension between B and C). By analogy, it follows that the original formula[21] which was incorrect for the three-center system formulated above (and in which the sign of the cosine term is positive), applies to the three-center system in which the motion about B is symmetrical rather than asymmetrical, *i.e.*, to the

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[15] H. C. Urey, *J. Chem. Soc.*, 562 (1947).

[16] Use of figures for C^{12} and C^{13} is required because the carbon isotope content of the carbon monoxide fraction is unaffected by combustion and the comparison of either carbon or oxygen isotope contents of carbon dioxide and carbon monoxide by direct mass spectrometric measurements is very imprecise due to differences between these two gases of the effect of isotope substitution upon ionization probabilities.

[17] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

[18] J. Bigeleisen and M. G. Mayer, *ibid.*, **15**, 261 (1947).

[19] J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

[20] N. B. Slater, *Proc. Roy. Soc.* (*London*), **194**, 113 (1948).

[21] J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1972 (1953).

[22] J. Bigeleisen and M. Wolfsberg, *ibid.*, **22**, 1264 (1954).

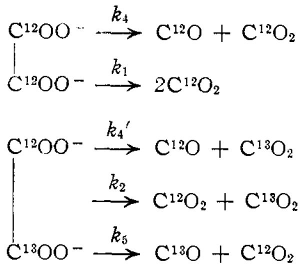
three-center situation in which both A–B and B–C bonds are being made or broken.[23]

In application of the three-center model it is assumed that a single vibration gives rise to the motion in the reaction coördinate, most simply either the symmetric or asymmetric mode in the imaginary triatomic system ABC.

In an earlier publication[24] it was shown that one could obtain, from isotopic rate constant ratio data taken over a sufficiently wide range of temperatures, a value for μ of reasonable precision. Since knowledge of this quantity permits direct computation of the temperature dependent part of such ratios, it is of interest to speculate on the information concerning the differences between the vibrational motions of the reactant and activated states which can be derived from such calculated results.

As detailed by Bigeleisen and Wolfsberg,[21] the vibration lost upon activation generates the quantity μ. Now, it will be possible usually to calculate the temperature dependent part of a ratio of isotopic rate constants in terms of a single frequency, which may have no relation whatsoever to any actual vibrational frequency in the reactant molecule or activated complex, and its isotopic companion, *i.e.*, in terms of an ω and a value for the ratio ω/ω_i (the subscript i denoting the frequency in the molecule labeled with the heavier atom of the isotopic pair).[25] Two simple approaches suggest themselves. First, one could set ω/ω_i equal to μ, then calculate the value of ω required to reproduce the observed temperature dependence; this is what has been done in some two-center cases.[8,19] Second, one could set up a three-center or more complicated model for the reaction, and employing distances, angles and force constants of reasonable magnitudes, compute a set of ω's and ω_i's. An appropriate value of ω/ω_i is estimated by comparison of the various normal modes of the model with the reaction coördinate motion assumed; the estimated ω/ω_i is then used in the calculation of a value for the ω to be lost upon activation which will reproduce the observed temperature dependence. The utility of the calculation lies in the possible similarity of this artificial ω to that for some normal mode in the model or the actual reactant molecule which involves motion like that in the assumed reaction coördinate. Where such similarity is observed one would take some confidence in the choice for reaction coördinate motion; were such correspondence not observed, the calculation would not have yielded a helpful result.

Intra-ionic Competition Models.—The simplest model for the decomposition of oxalate ion into two molecules of carbon dioxide is the two center C–C system; the competing process yielding carbon monoxide and carbon dioxide will be treated as a C–O two-center system in which C–C bond rupture follows the rate-determining oxygen abstraction, as a C–C–O three-center system involving symmetric motion, and as the O–C–O or C–O–Pb triads involving asymmetric motion. The following notation is adopted for the several rate constants



$$\begin{array}{ll} \mathrm{C^{12}OO^-} \xrightarrow{k_4} \mathrm{C^{12}O + C^{12}O_2} & \\ \mathrm{C^{12}OO^-} \xrightarrow{k_1} \mathrm{2C^{12}O_2} & \\ & (1) \\ \mathrm{C^{12}OO^-} \xrightarrow{k_4'} \mathrm{C^{12}O + C^{13}O_2} & \\ \qquad\quad \xrightarrow{k_2} \mathrm{C^{12}O_2 + C^{13}O_2} & \\ \mathrm{C^{13}OO^-} \xrightarrow{k_5} \mathrm{C^{13}O + C^{12}O_2} & \end{array}$$

It is impossible to obtain the appropriate ratios of these isotopic rate constants from the data available. We choose to assume values for k_1/k_2 and with the average values for R_r at each temperature calculate k_4/k_5, or other related ratio; we then compute the temperature independent part of k_4/k_5, examine its value in terms of some simple models, then carry out a very approximate treatment of the temperature dependent part.

Where a three-center model for the process competing with C–C bond rupture contains only one of the carbon atoms, $k_4/k_4' = 1$; if both of the carbon atoms are involved, as in a C–C–O system, this ratio will depend upon the relative involvement of the C–C and C–O bonds in the reaction coördinate motion, *i.e.*, upon the value of the parameter p. For $p = 0.3$ or less, the values of μ for k_4/k_4' are not very different from unity (Fig. 2, curve C), which suggests that k_4/k_4' is near unity in this range; in the whole range of p from 1 to ∞ the ratio of the μ's for k_4/k_4' and k_4/k_5 (Fig. 2, curves C and B, respectively) deviates from unity less than does that for k_4/k_4' at $p = 0.3$. As a matter of convenience, then, we make the following approximations: for p small compared with unity, $k_4/k_4' = 1$ and $k_4/k_5 \neq 1$; from $p = 1$ to ∞, $k_4/k_4' = k_4/k_5 \neq 1$.

In performing the integrations and in the equations below for R_r we employ the approximation $Y = 1 + (k_1/2k_4)$; this generates an error in R_r smaller than that due to imprecisions in the mass spectrometric measurements. For situations where one carbon atom is involved in the three-center model, where a C–O two-center model is considered, or where p is small for the C–C–O three-center model

$$R_r = \frac{C\left[\frac{M}{D} + 2\right]\left[2A_0\left(\frac{M}{D} + \frac{2}{C} + 2\right) + B_0(M + 4)\right]}{\left[2A_0(M + 2)\left(\frac{M}{D} + \frac{2}{C} + 2\right) + B_0(M + 4)\left(\frac{M}{D} + \frac{2}{C}\right)\right]} \quad (3)$$

where $M = k_1/k_4 = 2(Y - 1)$, $D = k_1/k_2$, $C = k_4/k_5 = k_4'/k_5$, A_0 = mole fraction of C^{12}–C^{12} oxalate in the original material, and B_0 = the corresponding mole fraction for C^{12}–C^{13} oxalate.[26] For the three center C–C–O model with p between 1 and ∞

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[23] J. Bigeleisen, *Can. J. Chem.*, **30**, 443 (1952).

[24] P. E. Yankwich and H. S. Weber, THIS JOURNAL, **78**, 564 (1956).

[25] This statement is a generalization to complicated models of a practice already found to be successful in two-center systems[19]: there a stretching frequency of the bond ruptured is presumed lost and, following the diatomic molecule argument,[20] ω/ω_i is taken as the ratio of the reduced masses of the imaginary atom pairs.

[26] Neglect of the oxalate species C^{13}–C^{13} introduces imperceptible error.

$$R_r = \frac{\left[\frac{M}{D} + \frac{2}{C}\right]\left[2A_0\,C\left(\frac{M}{D} + \frac{4}{C}\right) + B_0(M + 4)\right]}{\left[2A_0(M + 2)\left(\frac{M}{D} + \frac{4}{C}\right) + B_0\left(\frac{M}{D} + \frac{2}{C}\right)(M + 4)\right]} \quad (4)$$

where $C = k_4/k_5 = k_4/k_4'$, but the other symbols have the same meaning as in equation 3.

In Fig. 3 are plotted as functions of temperature values of k_4/k_5 derived from the experimental data by application of equations 3 and 4; curves C and C′ show the relative insensitivity of the k_4/k_5 values to that assumed for the frequency of the C–C stretching vibration. The temperature dependence of k_4/k_5 as graphed in curve A is very large for an isotope effect of that magnitude; further, the values of μ obtained from the curve range smoothly from 1.009 at $(1000/T) = 1.5$ to 1.018 at $(1000/T) = 1.1$. The temperature dependent part of k_4/k_5 calculated by equation 4 exhibits a similar anomalous dependence upon temperature. For these reasons we reject the C–C–O three-center model involving asymmetric motion and large values of p.

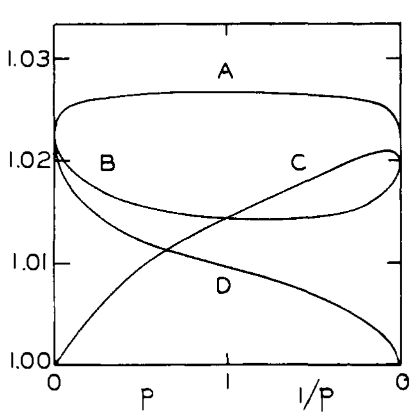

Fig. 2.—Temperature-independent factor, μ, in isotopic rate constant ratio as a function of p.[21] For asymmetric motion about B, curves A and D:

$$\mu = \left[\frac{(m_B{}^{-1} + m_C{}^{-1}) + p(m_B{}^{-1} + m_A{}^{-1}) - 2p^{1/2}m_B{}^{-1}(\cos \mathrm{ABC})}{(m_{B_i}{}^{-1} + m_{C_i}{}^{-1}) + p(m_{B_i}{}^{-1} + m_{A_i}{}^{-1}) - 2p^{1/2}\,m_{B_i}{}^{-1} \times (\cos \mathrm{A_iB_iC_i})}\right]$$

for symmetric motion, curves B and C, the minus sign to the cos term is replaced with +. Curve A, O–C–O system: $\mathrm{ABC} = \mathrm{A_iB_iC_i} = 120°$; $m_A = m_{A_i} = m_C = m_{C_i} = 16$; $m_B = 12$, $m_{B_i} = 13$. Curve B, C–C–O system: $\mathrm{ABC} = \mathrm{A_iB_iC_i} = 120°$; $m_A = m_{A_i} = m_B = 12$; $m_{B_i} = 13$; $m_C = m_{C_i} = 16$. Curve C, C–C–O system: $\mathrm{ABC} = \mathrm{A_iB_iC_i} = 120°$; $m_A = m_B = m_{B_i} = 12$; $m_{A_i} = 13$; $m_C = m_{C_i} = 16$. Curve D, Pb–O–C system: $\mathrm{ABC} = \mathrm{A_iB_iC_i} = 180°$; $m_A = m_{A_i} = 207$; $m_B = m_{B_i} = 16$; $m_C = 12$, $m_{C_i} = 13$.

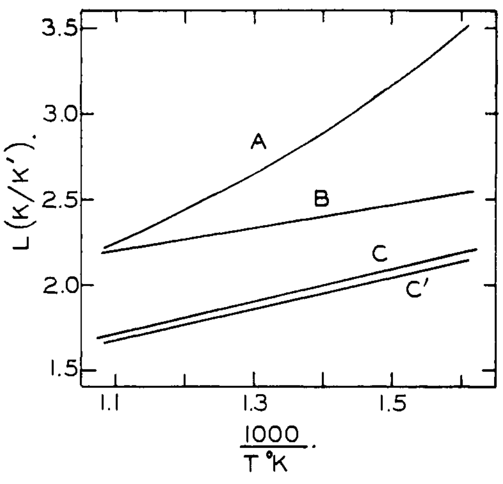

Fig. 3.—Calculated isotopic rate constant ratios; $L(k/k')$ *versus* $1000/T$°K., $L = 100\ ln$. Curve A, k_4/k_5 by equation 4; values for k_1/k_2 taken from curve B. Curve B, k_1/k_2, two-center model; $\mu = \omega/\omega = 1.0198$, $\omega_{C-C} = 850$ cm.$^{-1}$. Curve C, k_4/k_5 by equation 3; values for k_1/k_2 assume $\omega_{C-C} = 850$ cm.$^{-1}$. Curve C′, k_4/k_5 by equation 3; values for k_1/k_2 assume $\omega_{C-C} = 750$ cm.$^{-1}$.

We consider seriatim the four models described above for the oxygen atom abstraction process competing with simple C–C bond rupture. The values of μ obtained for k_4/k_5 from curves C and C' are 1.0138 and 1.0134, respectively; if these values are assumed for ω/ω_i, the artificial frequency ω is calculated to be 1220 cm.$^{-1}$ for curve C and 1230 cm.$^{-1}$ for curve C′. Each of these groups of μ, ω/ω_i and ω values reproduces the plot of calculated k_4/k_5 within ±0.0005 over the temperature range covered by the experiments. The C–C stretching force constant in oxalate ion[27] leads to a calculated stretching frequency near 700 cm.$^{-1}$, and we adopt a value of 1.014, for the μ of k_4/k_5. The values of μ for the C–O two-center system and for asymmetric motion in the O–C–O system with bond angle (120°) near that observed for crystalline oxalates (Fig. 2, curve A) are equal to or greater than 1.0227, leading to rejection of these models. The calculated μ for symmetric motion in the C–C–O system (Fig. 2, curve B) is close to 1.014 for values of p in the vicinity of unity; however, the original approximations leading to equations 3 and 4 require that p be less than 0.2–0.3 in the present instance, so this model is unsatisfactory. Consideration of the vibrations of C–C–O would lead us to the same end, for with force constants of reasonable magnitude chosen for this fragment of the oxalate ion a temperature dependent part of k_4/k_5 is predicted which is much larger at all temperatures than that "observed" (*i.e.*, than that calculated on the basis that k_1/k_2 is appropriately estimated in terms of the C–C two-center model).

We consider finally the linear C–O–Pb triad, for which values have been plotted in Fig. 2, curve D, the motion assumed being asymmetric. In this case we are not limited by the kinetics analysis to p values in any particular range, and the calculated value of μ for the system becomes 1.014 near $p = 0.3$, which implies that the amount of bond extension between C and O is about twice the amount of bond formation between O and Pb. This bond involvement situation seems reasonable for such an oxygen atom transfer. Less clarity is evident when we consider the temperature dependent part of k_4/k_5 which one calculates for this model. The *reactant* state requires consideration only of the stretching vibration between the carbon and oxy-

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[27] F. Douville, C. Duval and J. Lecomte, *Bull. soc. chim. France*, **9**, 548 (1942); see also H. Murata and K. Kawai, *J. Chem. Phys.*, **25**, 589 (1956).

gen atoms. In the activated complex the symmetric stretching and bending vibrations must be considered, the asymmetric vibration being assumed similar to the reaction coördinate motion and, therefore, having given rise to μ. Since the reactant state is represented by a two- and the transition state by a three-center model, the argument presented above concerning comparison between a normal mode of the reactant state model and the assumed reaction coördinate motion is applied in a different sense, *viz.*, that correspondence is sought between the latter and a normal vibrational mode which the activated complex would exhibit *if* the vibration leading to increase in the reaction coördinate were ordinary. By juggling the properties of the C–O–Pb system one can produce agreement with the temperature dependence of k_4/k_5 using a group of force constants and distances having reasonable magnitudes, provided that the asymmetric normal mode is selected as the reaction coördinate motion.

An alternate choice for the process leading to C–C bond rupture is asymmetric motion in the three-center system C–C–O, bond extension taking place between C and C, and bond formation between C and O. In effect this adds still another parameter to the over-all picture, *i.e.*, p for this triad, and does not further illuminate the situation.

In Table I the total change in $R^0_{CO_2}$ is only $(11 \pm 5) \times 10^{-6}$; for none of the models considered above is the change predicted in O^{18} content of product carbon dioxide outside the limits defined by this figure. Thus the O^{18} isotope effect is not a useful adjunct to evaluation of these models.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE WASHINGTON UNIVERSITY]

Electron Spin Resonance Study of the Electron Exchange between Naphthalene Negative Ion and Naphthalene[1]

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The rate of the electron exchange reaction between naphthalene negative ion and naphthalene has been determined by a spectroscopic method. Broadening of the electron spin resonance lines of naphthalene negative ion occurs in the presence of naphthalene. Bimolecular rate constants are deduced from the variation of line breadth with concentration of added naphthalene. The rate constants vary with solvent and with the choice of positive ion. They lie in the range 10^7–10^9 liter mole^{-1} sec.$^{-1}$.

Introduction

The rate of a chemical reaction is usually determined by a sequence of measurements in time of properties which vary as the reaction proceeds. Such measurements yield directly the net changes in the quantities of reactants and products. Individual rates of production and consumption are inferred from the net rates and these inferred rates are sometimes subject to considerable uncertainties. Direct determination of rates of production and consumption of participants in a reaction has become possible in certain cases by the recent development of radiofrequency and microwave spectroscopic techniques of high resolving power.

The measurements depend on the fact that the shape of a spectroscopic line associated with a transition between a pair of states is affected by the mean life of the states. The essential ideas involved in the relations between lifetimes and line breadths were worked out by Lorentz in his treatments of the effects of collisions on the breadth of spectral lines.[3] Many authors have further developed the subject.[4–11] The theoretical treatment of P. W. Anderson[8a] appears to be the most readily applicable to the interpretation of the kinds of experiments which we shall describe here.

These experiments consist of observations of the electron spin resonance spectra of naphthalene negative ion (to be referred to as naphthalenide) in the presence of naphthalene.

In the concentration range 10^{-4}–10^{-3} M in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), the spectrum of naphthalenide consists of a set of seventeen hyperfine components extending over a field interval of 27.2 oersteds. The breadth of each line is about 0.9 oersteds between points of extreme slope. This description applies to the spectrum of lithium, potassium, rubidium or cesium naphthalenide. Sodium naphthalenide, on the other hand, behaves differently. In DME its spectrum is

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(2) E. I. du Pont de Nemours Post-Graduate Fellow, 1955–1956.

(3) H. A. Lorentz, *Proc. Acad. Amst.*, **8**, 591 (1906).

(4) (a) V. Weisskopf, *Z. Physik.*, **75**, 287 (1932); (b) J. H. Van Vleck and V. Weisskopf, *Rev. Mod. Phys.*, **17**, 227 (1945).

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(10) J. T. Arnold, *ibid.*, **102**, 136 (1956).

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