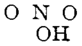
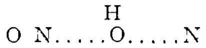
Br^- reacting with HOCl is almost 20 times that for Cl^- substituting on Cl in HOCl. The relatively higher rate for Br^- reacting with HOCl suggests a different site of attack for Br, which therefore must be on oxygen.

This conclusion, by no means certain for the present system, is important to the problem of the role which H^+ may play in reactions of oxy-ions. The only reasonable place for the proton in the activated complex of composition $(HOClBr)^-$ is on oxygen. If then Br^- attacks O rather than Cl in HOCl, the role of H^+ in labilizing O for transfer is demonstrated. Definite evidence for this conclusion is found in work with the Br^-–HOBr system. The exchange of Br between Br^- and HOBr[14] is found to be more rapid than the Br^- catalyzed oxygen exchange of HOBr, thus demonstrating directly that Br^- attacks oxygen in HOBr. The particular function of protons in the activated complex for reactions of anions which has been described is suggested also by observations on other systems. Thus, pernitrite persists in alkaline solution but in acid is transformed rapidly to NO_3^-.[15] A reasonable formulation for the activated complex in question is



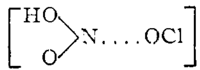
$$\underset{OH}{ONO}$$

The activated complex providing for rapid exchange[16] of NO with NO_2^- involves H^+. Here also, the location of the proton on a bridge oxygen seems the most reasonable possibility



$$ON\ldots\overset{H}{O}\ldots NO$$

Attempts were made in the course of the present work to decide between the activated complexes



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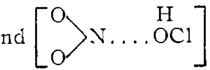

L

for the reaction of NO_2^- with hypochlorite by studying the rates of reaction of RONO + OCl^- and NO_2^- with ROCl. Using an aliphatic group for R, the reaction of nitrite ester is found to be very slow. On the other hand, the reaction of the hypochlorite ester with NO_2^- is very rapid, but only a small fraction proceeds to the product $RONO_2$ expected for formulation L. This being so, the experiment must be regarded as inconclusive on the point under consideration (a small amount of $RONO_2$ may appear as a side reaction of the principal change occurring), although it is consistent with formulation L for the activated complex.

Acknowledgments.—This work was supported by the Office of Naval Research under Contract N6-ori-02026. The funds for the purchase of the mass spectrometer used in the research were supplied by the Atomic Energy Commission under Contract At(11-1)-92.

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(14) M. Anbar and R. Rein, to be published.

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(16) M. Anbar and H. Taube, to be published.

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The Measurement of Very Slow Reaction Rates; Decarboxylation of Alanine[1a]

BY DWIGHT CONWAY[1b] AND W. F. LIBBY[1c]

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A method of measuring slow reactions using radioactive labelling and low level counting techniques has been applied to the decarboxylation of alanine at temperatures corresponding to half-lives from 0.1 to 10^4 years, the results being essentially in agreement with those which Abelson obtained at higher temperatures. The half-life for decarboxylation at room temperature is found to be about 10 billion years. A side reaction, which is most probably a short chain length radiation induced reaction, was controlling below 373°K. and showed a half-life of about 10^5 years at room temperature at our specific radioactivities of about 3 millicuries of C^{14} per mole of alanine. It also was found that O_2 attacks alanine to release carboxyl carbon at a rate corresponding to a half-life of about 20000 years at room temperature.

Introduction

A Few Possible Applications of the Method.—By the use of radioisotopes the rate of very slow reactions can be measured.[2] Many reactions which proceed by very complicated mechanisms at high temperatures should take place by much simpler mechanisms at low temperatures since in competing branch reactions the high activation energy process will be "frozen out," *e.g.*, the reaction of H with O_2 gives all HO_2 and no HO plus O at low temperatures. There would be no reactions of product with product molecules because of the very low concentration of products. Also in some cases the increased stability of the products at low temperatures would simplify the mechanism. A knowledge of the low temperature mechanism should provide information (activation energies and steric factors) which would aid in understanding the high temperature mechanism.

Therefore, the application of the method to the study of many reactions should prove fruitful. Many practical applications to such problems as food spoilage probably can be made by study of especially cultured radioactive natural products.[3]

The method constitutes a powerful tool for the study of very slow reactions. In addition to the

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(1) (a) This research was supported in part by the Office of Scientific Research of the Air Research and Development Command, U. S. Air Force Contract No. AF 18(600)-663; (b) now at Chemistry Department, Purdue University, Lafayette, Indiana; (c) presently a Member of the U. S. Atomic Energy Commission.

(2) W. H. Johnston and P. J. Manno, THIS JOURNAL, **79**, 807 (1957).

(3) N. J. Scully, W. Chorney, G. Kostal, R. Watanabe, J. Skok and J. W. Glattfeld, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy in Geneva," Vol. XII, 1955, p. 377.

applications to fundamental research on reaction kinetics, important practical applications probably can be made to the study of the rate of oxidation of paper, rubber, cloth, etc., as well as to the spoilage of food and similar problems. The radioactive materials needed for such applications can be prepared by biosynthetic techniques similar to those used on the Isotope Farms at the Argonne National Laboratory and at the Medical College of Virginia. The limitation of the method is, of course, the reaction induced by the radiation from the radioactive substances being studied, but it seems very probable that this is not serious for many applications both practical and fundamental.

Theory.—Suppose n moles of a reactant in a reaction is "tagged" with A disintegrations per minute (d.p.m.) of radioactivity in a particular atomic position appropriate for the reaction being studied and the reaction carried out as usual. Since the method is applied to very slow reactions, only a small amount of a certain product, Δn moles, is formed in the time Δt, and this contains a small amount of radioactivity, ΔA d.p.m. If the isotope effect is neglected, the radioactive concentration is the same in the reactant as in the product, *i.e.*

$$A/n = \Delta A/\Delta n \qquad (1)$$

From (1) the rate at which the "tagged" reactant generates the certain product in moles/l.sec. is given by (2)

$$\Delta n/(V \times \Delta t) = n \times \Delta A/(V \times A \times \Delta t) \qquad (2)$$

where Δt is in sec. and n/V is the concentration of the "tagged" reactant in moles/l. By the use of this equation the order of the reaction with respect to each of the reactants can be measured by "tagging" only one reactant.

From eq. 2 without the V's it is shown easily that the initial half-life, $t_{1/2}$, for formation of the detected product is given by

$$t_{1/2} = 0.693 \times A\ (\Delta t/\Delta A) \qquad (3)$$

The half-life calculated by eq. 3 will be constant for any value of Δt for very slow reactions since the concentration of reactants remains essentially constant throughout the reaction. However, the half-life will be a function of the concentration(s) of the reactant(s) unless the reaction is first order. From the variation of the half-life the order of the reaction with respect to each reactant can be determined by varying the concentration of one reactant at a time. This half-life is the half-life for reaction of the "tagged" reactant alone, and, therefore, may be somewhat different from that of the untagged reactant due to isotope effect—possibly a factor of 20 larger in the extreme case of tritium compared to ordinary hydrogen, and probably about 10% larger in the case of C^{14} as compared to C^{12} in most organic compounds and even less for heavier elements.

Radiation Damage.—An obvious potential limitation of the method is that the radiation emitted by the radioactive isotopes used for the labelling may in itself cause reactions which could be confused with the reaction intended for measurement. The half-life for this radiation damage reaction, $t_{1/2r}$, is to be calculated as follows. The rate in moles/year for the formation of the "tagged" product molecule by radiation damage for molecules containing not more than one radioactive atom per molecule is given by eq. 4.

$$(\Delta n/\Delta t)_r = 8.74 \times 10^{-15}\ AEG \qquad (4)$$

where E is the average radiation energy per disintegration in Mev. absorbed by the sample, G is the number of product molecules generated per 100 e.v., and the isotope effect has been neglected. For β-radiation, E generally is about 40% of the maximum energy of the β-spectrum. From the usual relation between the half-life and the rate of a unimolecular reaction, $t_{1/2r}$ (years) is

$$t_{1/2r} = 7.93 \times 10^{13}(n/A)EG \qquad (5)$$

where n is the number of moles of the "tagged" reactant. The values of G normally reported in the literature for various radiation induced reactions range up to 100.[4] In order to measure very long half-lives, the background radiation damage reaction rate must be kept very low, so the radioactive concentration, A/n, must not be so large as to cause the radiation induced reaction to interfere with the reaction being investigated. From eq. 3 it is seen that the lower the A, the smaller must be ΔA since it is inconvenient to have Δt, the length of the experiment, longer than about 0.1 year. This means that a sensitive detecting device should be used to measure the very small ΔA's, hence low level counting techniques may be necessary.[5]

For example, if an organic compound were to contain 1% of its carbon atoms as C^{14} (half-life 5600 years; E, 0.045 Mev.[6]) and a G value of 100 is assumed, the radiation induced half-life would be 12 years so reactions at rates slower than this could not be measured with such a preparation and dilution would be necessary.

Decarboxylation of Alanine.—The decarboxylation of alanine was selected for study because of its geophysical interest.[7] The previous work of Abelson[7] at higher temperatures assured a basis of comparison.

Experimental

Description of the Radioactive Alanine Samples. *dl*-α-Alanine-1-C^{14} from Tracerlab[8] was diluted with Eastman *dl*-α-alanine so that the radioactive concentration was about 0.02 to 0.1 mc./g. of alanine (A/n value of 0.4 to 1.9×10^{10} d.p.m./mole; 4.6 to 23 μg. C^{14}/g.; or 0.0011 to 0.0057% C^{14} in carbon in alanine). This alanine was crystallized from an aqueous solution by the addition of ethyl alcohol, vacuum dried, and stored in a vacuum desiccator. Various research samples were prepared from this alanine, together with conductivity water, and analytical reagent grade Na_2SO_4 and $NaHSO_4$. The reaction tubes were generally cleaned previous to sample addition by condensing steam on their surfaces for several hours. The systems studied are described in Table I.

Temperature Regulation.—Two ovens were constructed by placing aluminum cups filled with bath wax inside 1.5 inch diameter Alundum cores wound with resistance heater wire and fitted with No. 17000 Fenwall thermoregulators mounted coaxially through the bottom of the ovens. The temperature, which was measured to ±0.1° with a chromel–

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(4) F. S. Dainton, *Ann. Rev. Nuc. Sci.*, **5**, 213 (1955).

(5) E. C. Anderson, J. R. Arnold and W. F. Libby, *Rev. Sci. Instr.*, **22**, 225 (1951).

(6) G. H. Jenks and F. H. Sweeton, *Phys. Rev.*, **86**, 803 (1952).

(7) P. H. Abelson, *Sci. American*, **195**, 83 (1956); *Science*, **119**, 576 (1954).

(8) Tracerlab, Inc., 1114 S. Michigan Ave., Chicago 5, Illinois.

TABLE I

RADIOACTIVE ALANINE SYSTEMS USED

Sample	Type of reacn. ves-sel	Phase	Alanine concn. (*m*)	$NaHSO_4$ (*m*)	Na_2SO_4 (*m*)	Vol. of soln. (ml.)
B	*a*	Solid				
I	*a*	Solid				
U	*a*	Solid				
C′[d]	*c*	Aqueous	0.17	0.5	0.5	650
J	*b*	Aqueous	.13			10
M	*b*	Aqueous	.17	.48	.47	10
O	*b*	Aqueous	.78			10
P	*a*	Aqueous	1.47			10
Q	*b*	Aqueous	1.10	.96	.92	10
R	*b*	Aqueous	1.55	.61	.33	20
S[e]	*b*	Aqueous	0.043			30

[a] Pyrex tube (19 mm. by 16 cm.) with ordinary stopcock. [b] Medium wall Pyrex tube (25 mm. by 19 cm.) with high-pressure stopcock. [c] One-liter flask 2 (Fig. 1). [d] Contains 0.1 *m* $SnCl_2$ and a Teflon boiling chip. [e] Surface area 210 ± 80 times that for Sample *J*.

P alumel thermocouple calibrated at the freezing point of tin and the boiling point of water, was regulated to ±0.5° for days in the air-conditioned laboratory and was constant to ±0.1° along the tube axis in the oven. Boiling water-baths also were used to control the temperature to ±0.7° for some 100° runs in the tubes. In the large flask 2 (Fig. 1) the vapor pressure was used to adjust the temperature to ±1.5°.

Reaction Procedure.—The reactions were conducted in the Pyrex vessels described in Table I (and its footnotes). The aqueous solutions were freed of air by careful evacuation after freezing with liquid N_2, melting and repeating the process. A known amount of carrier CO_2 (solid samples) or CO_2 and A (aqueous samples) purified of air, were added through a trap at −79° and the system held at the desired temperature for times of a few hours to 18 weeks. (The A served as a diffusion block at high temperatures to keep the water from heating the neck of the stopcock which projected from the oven.) At the end of this reaction period, the reaction vessel was cooled, reconnected to the vacuum line (Fig. 1) and the gaseous CO_2 separated and measured for C^{14}-content as described below. From these counting data, the total weight and specific radioactivity of the alanine sample used, an (apparent) half-life was calculated in each case.

Except for the B series of measurements on solid alanine in which the CO_2 was purified by sublimation from one liquid N_2 trap to another, the CO_2 and A were always purified by passing these gases at 500° twice through a Cu reduction tube (Item No. 6 in Fig. 1) composed of a 16 cm. length of Cu turnings with a 1.5 cm. plug in the center of Cu powder and silica gel. These precautions were necessary since oxidation of the alanine would produce radioactive CO_2 confusing the results.

In the B series for those runs at temperatures above 373°K. after removal of the C^*O_2 in the gas phase, water and carrier CO_2 were added to the tube and removed several hours later to take out the C^*O_2 trapped in the solid alanine. In the longest B series at 373°K., the activity in the gas phase was determined repeatedly over 80 days, and then the activity left in the solid alanine was determined. This latter procedure was used several times in succession on the other solid alanine samples (I and U series) except that water purified of air by vacuum distillation was distilled into the reaction tube.

In the runs made in the absence of carrier CO_2 to test the possibility of CO_2 exchange with the alanine, the CO_2 was added after the run, the solutions shaken, and the C^*O_2 removed several hours later for the solution runs.

At the conclusion of the J series on 0.13 *M* alanine aqueous solution, 20 ml. of conductivity water and 2.52 g. of Pyrex glass wool which had been soaked for 8 hours in CCl_4, rinsed in acetone, washed 5 times with hot water, and dried on a hot plate for 5 hours, were added to the tube to test for surface catalysis of the reaction. The surface area of the wool was calculated from the average diameter of the fibers obtained with a micrometer and a density of 2.2 for Pyrex to be 210 ± 80 times that for the reaction vessel itself. In the middle of this packed tube series (S) the temperature was raised to 408°K. for 164 hours and then returned to 373°K.

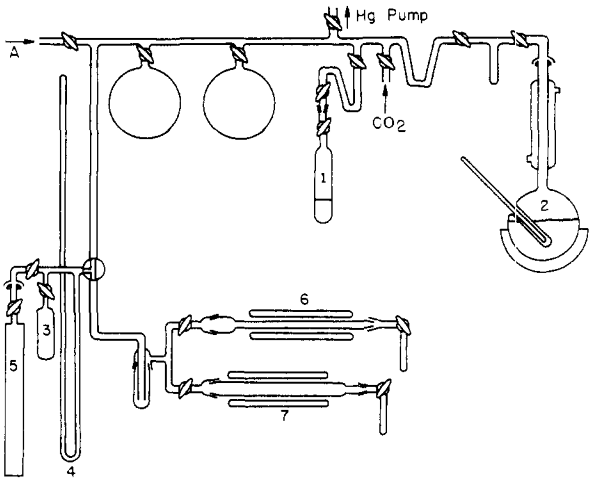

Fig. 1.—Vacuum line: (1) reaction tube with either solid alanine or aqueous solution; (2) reaction bulb for aqueous solution; (3) calibrated bulb for measuring quantity of CO_2; (4) mercury manometer; (5) Geiger counter; (6) Cu reduction tube for A and CO_2 purification of O_2, and (7) $Mg(ClO_4)_2$ drying tube.

Purification of the C^*O_2 and Counting.—The water impurity was usually removed from the C^*O_2 by subliming the C^*O_2 once from a liquid N_2 trap, passing it twice through the $Mg(ClO_4)_2$ drying tube 7 (Fig. 1), and distilling it once again, although sometimes it was simply purified by three distillations. The pressure of the C^*O_2 was then measured in order to correct for the loss of the gas during purification (about 10%), and 97% of the C^*O_2 was expanded into a Geiger counter (Item No. 5 of Fig. 1). About 1.5 cm. of thrice distilled C_2H_4 and 8 cm. of tank A or purified A were added to complete the counting gas mixture. The anticoincidence shield[8] was used for samples with less than 190 d.p.m., and a high level scaler was used for the other samples. The counting was done to ±0.5 to ±3% depending on the total activity. (Only once was ΔA less than 6 d.p.m.) A correction of 3.1% was applied for loss of activity at the counter ends and of 1.5% for wall loss.[9] At high levels a coincidence correction, which was less than 3% except for the B runs at 473°K., was applied (dead-time 4.5 × 10^{-6} minutes).

The Geiger counter was constructed from a brass cylinder (2″ × 18″) with Lucite ends sealed with Apiezon-W and a 2 mil tungsten center wire. After the brass cylinder was cleaned in 5 *M* HNO_3 and the counter constructed, CO_2 at 1 atm. pressure was left in the counter 24 hours to convert any surface oxide into the carbonate. Although this type counter slowly became contaminated, a contamination-proof counter composed of a Cu cylinder with a surface layer of CuS was constructed and used in several determinations.

Determination of Absolute Activity, *A*, of the Alanine.—Thick layers of the solid alanine samples of known area were measured with a 1.90 mg./cm.[2] Mylar covered flow counter with Q gas as the counting gas in the manner of Sugihara, *et al.*[10] The solid alanine samples were prepared from an aliquot of the radioactive alanine solution which was pipetted into a known amount of non-radioactive alanine, the whole amount of alanine dissolved, and the solution evaporated. Two such samples were mounted, counted, and the specific activity of the solution calculated by the use of eq. 6

$$s = \frac{CR}{A} \qquad (6)$$

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(9) A. G. Engelkemeir and W. F. Libby, *Rev. Sci. Instr.*, **21**, 550 (1950).

(10) T. T. Sugihara, R. Wolfgang and W. F. Libby, *ibid.*, **24**, 511 (1953).

where s is the specific activity of the alanine in d.p.m. per mg., R is the count rate (counts per minute—c.p.m.) after correction for background and coincidence loss, and A is the sample area in cm.^{2}. The constant C can be calculated[11] to about 5% accuracy. Direct determination was made, however, by taking 5.00 ml. of the original solution, diluting it to 25.0 ml., and vacuum distilling the water from two aliquots. The residual alanine samples were then oxidized by heating with CuO mixed with and placed over the solid. The C^*O_2 was purified as usual, and counted. (The yield of C^*O_2 was 104 ± 4% of theoretical which proved that the alanine was completely oxidized.) From the results given in Table II, C was calculated to be 2.17.

TABLE II

CALIBRATION OF THE SOLID COUNTING PROCEDURE

A. Solid counts

Ml. of soln.	R, c.p.m.	A, cm.^{2}	Wt. of alanine, mg.	(d.p.m./ml.)10^{-4}
5.00	1126	21.6	1046	1.09C
10.00	2140	29.6	1561	1.13C
			Av.	1.11C

B. Gaseous CO_2 counts

Ml. of soln.	R, c.p.m.	A, cm.^{2}	Wt. of alanine, mg.	(d.p.m./ml.)10^{-4}
0.200	2990			2.43
0.160	3480			2.39
			Av.	2.41

By the use of this value of C and the very same counting geometry, the specific activity of all further alanine samples were determined by solid counting them. It is believed that the relative values of the half-lives are good to ±5%, whereas the absolute values are good to about ±15%.

Results

Solid Phase (Runs B, I and U).—The solid alanine samples were heated in Pyrex tubes with ordinary glass stopcocks for periods up to 80 days (Fig. 3) at temperatures from 100 to 200°. The results are given on the general Arrhenius plot of the half-lives against $1/T$ (Fig. 2).

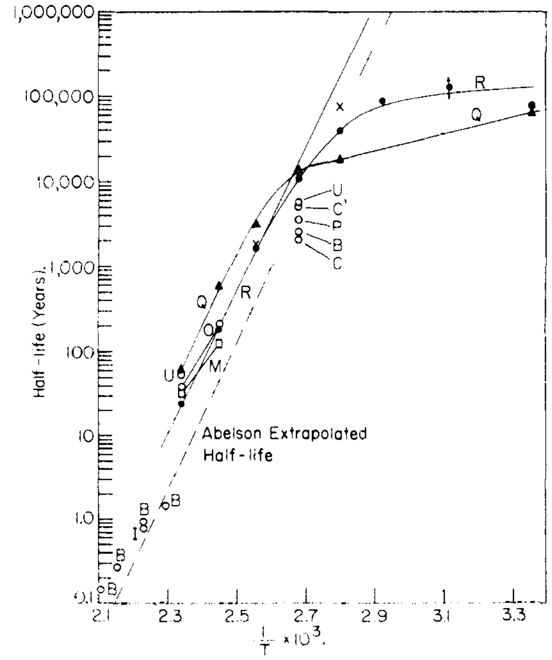

Fig. 2.—Arrhenius plot of the alanine decarboxylation half-lives.

The method used for the B samples suffered from the fact that O_2 was present in the water when it was added to the tube in order to remove the C^*O_2 from the solid alanine, so traces of O_2 remained which reacted with the alanine on the succeeding run. (See Oxygen Effect.) At 373°K. the half-lives varied from $^1/_{120}$th to $^1/_{40}$th of Abelson's extrapolated values in aqueous solutions[7] as the length of the run (Δt) was varied from 13 to 93 hours. Therefore, the B high temperature results plotted in Fig. 2 which are for single rate determinations except for two determinations at the highest temperature are lower limits to the true ones, and the lower the temperature, the less trustworthy are the half-lives because the oxidation reaction has the lower activation energy. The low temperature 373°K. (2.67×10^{-3} $1/T$ value) result in the B series was obtained in a single run for 80 days. For this run, the apparent half-lives as calculated from the average rate of C^*O_2 evolution into the gas phase at the indicated time are plotted in Fig. 3. During the last 50 days, the apparent half-lives increased with a half-life of 50 days, *i.e.*, during the 50 days they increased a factor of two. The rate of diffusion of C^*O_2 from the crystal mass apparently continuously decreased during the run probably due to crystal growth. At the end of the run at 80 days the total C^*O_2 in the solid phase was determined and added to the integral amount of activity obtained over the last part of the curve in Fig. 3. This procedure, by which a correction was made for much of the initial O_2 oxidation effect, gave the value for the half-life at 373°K. of 2550 years which is plotted in Fig. 2. This should be taken as a lower limit, since some oxidation effect may have remained.

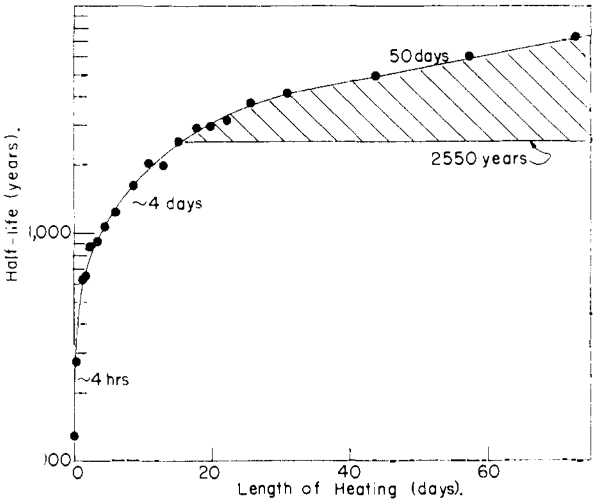

Fig. 3.—Solid alanine apparent half-lives from C^*O_2 diffusing out of solid at 373° (B sample).

A similar procedure was performed five times in the I series at 449°K. except that O_2-free water was distilled into the tube at the end of each run to extract the C^*O_2 from the solid alanine (Fig. 4). In the last three runs the co-linear curves III, IV and V were obtained with half-lives of 1.08, 0.86 and 1.14 years, where the C^*O_2 left in the crystals was added in at the end of the runs. From the reproduction obtained in the last series of experi-

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[11] A. D. Suttle, Jr., and W. F. Libby, *Anal. Chem.*, **27**, 921 (1955); W. F. Libby, *ibid.*, **29**, 1566 (1957).

TABLE III

HALF-LIVES IN YEARS FOR THE AQUEOUS SAMPLES

Sample	426.6°K.	407.8°K.	391.0°K.	373.1°K.
C′				5100
J				
M	33.7 ± 0.4 (3)	133 (1)		
O	39.3 ± 3.2 (4)	202 ± 13 (8)		
	26.8 ± 3.4 (13)	115 ± 2 (3)		
P				3500
Q	42 (1)	236 ± 12 (3)	1300 ± 110 (2)	6300 (1)
	53.7 ± 3.1 (6)	396 ± 33 (7)	2180 ± 90 (2)	9700 ± 560 (2)
	62.5 ± 2.8 (4)	495 ± 7 (4)	2450 ± 57 (3)	9960 ± 1500 (2)
	58.1 ± 9.6 (6)	577 ± 20 (4)	3040 ± 90 (5)	13900 ± 400 (4)
R	28.7 ± 2.1 (2)	150 ± 9 (4)	640 ± 100 (3)	
	27.2 ± 1.2 (5)	158 ± 7 (5)	932 ± 104 (5)	1980 ± 380 (7)
	27.2 ± 1.6 (5)	165 ± 13 (6)		4140 ± 590 (10)
	25.1 ± 0.14 (3)	173 ± 8 (3)	1528 ± 29 (4)	9320 ± 680 (5)
	25.5 ± 0.8 (5)	196 ± 12 (8)	1840 ± 120 (7)	11000 ± 570 (7)
	23.0 ± 1.0 (3)	191 ± 6 (8)	1562 ± 115 (8)	9900 ± 370 (5)
Sample	357.2°K.	342.2°K.	320.3°K.	298.2°K.
C′				
J				58000 (1)
M				
O				
P				
Q	19600 (1)			
	18300 (1)			64000 ± 15000 (1)
R	39000 ± 5700 (3)	92000 ± 12000 (3)	186000	
	39400 ± 1700 (3)	79000 ± 5000 (3)	97000 ± 12000 (2)	72000 (1)

ments it appears that this method probably gives a fairly accurate measure of the half-life at 449°K. although it probably is closer to 1.2 years than the average of the last three determinations.

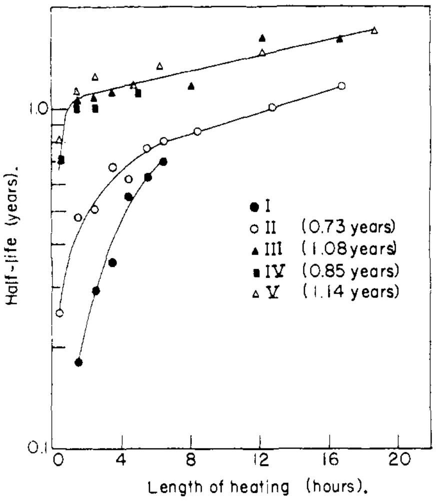

Fig. 4.—Solid alanine apparent half-lives from C^*O_2 diffusing out of solid at 449°K. (I sample).

In the U sample a series of experiments lasting 2 weeks gave a half-life of 53 years at 427°K. after treating the data in the same manner as with the I sample. Successively longer half-lives between 180 and 1900 years were obtained at 373°K. for 7 runs lasting one week each. Then a final run was made during 11 weeks in which a half life of 5550 years was obtained (Fig. 2).

Oxygen Effects.—The unbuffered aqueous solution of 0.13 *M* concentration (J series) half-lives at 373°K. were determined as a function of the total length of heating from the time the solution was last exposed to air for 1000 hours. Then 0.8 cm. of Matheson O_2 purified by one distillation from a liquid N_2 trap was added to the reaction tube. The half-life decreased to 4.5 years (Fig. 5). The large decrease confirmed the expected high rate of oxidation.

Aqueous Solutions (Runs C′, J, M, O, P, Q, R and S).—The results for the aqueous solutions are given in Table III, Fig. 2 and Fig. 6, most of

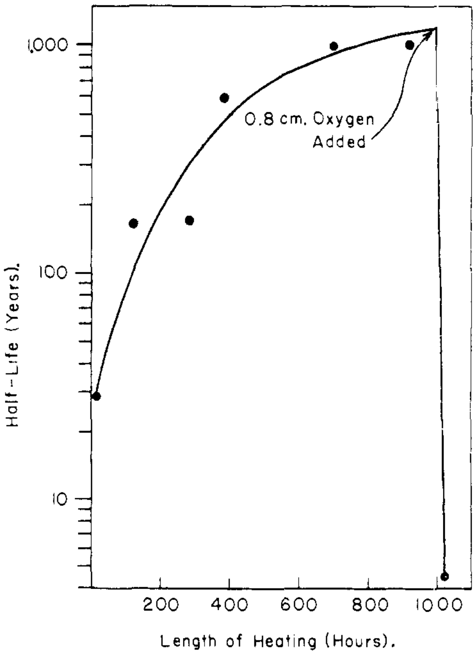

Fig. 5.—Aqueous alanine solution (0.13 *M*) half-lives *vs.* time at 373°K.; effect of added O_2 (0.8 cm. pressure).

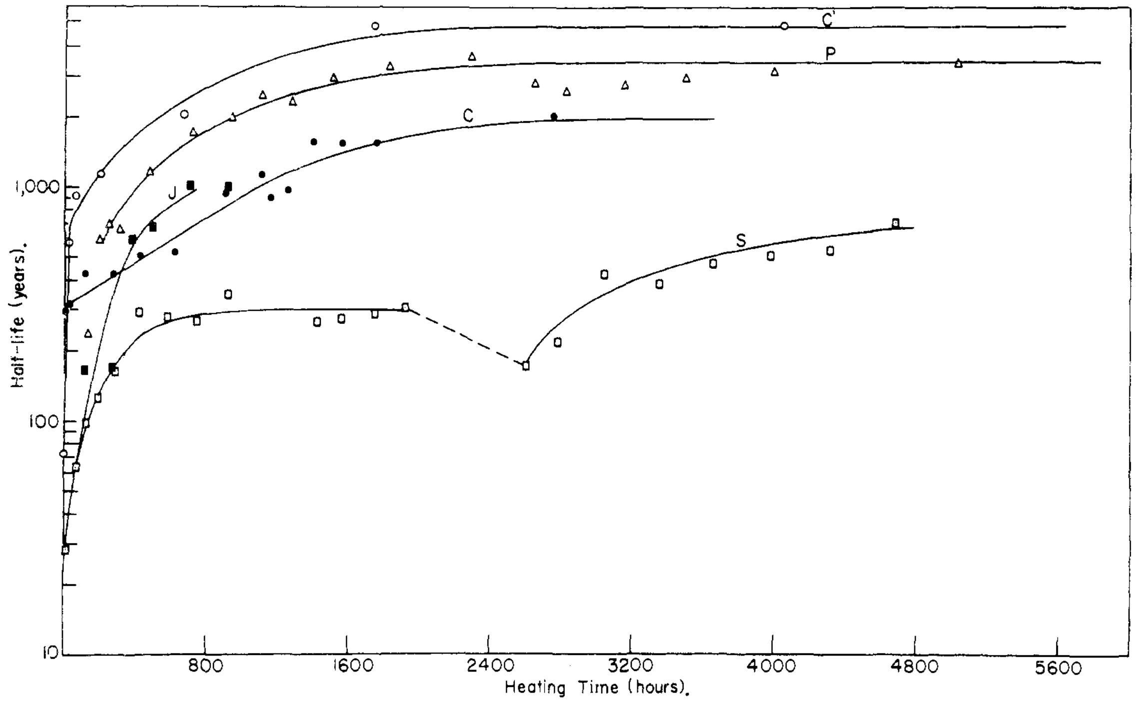

Fig. 6.—Decarboxylation half-lives for aqueous alanine solutions (about 0.1–1.5 *M*, *cf.* Table I) at 373°K. *vs.* time.

the 373°K. data (C′, J, P and S series) being plotted in Fig. 6. (Curve C in Fig. 6 results from experiments on solution C′ previous to the addition of $SnCl_2$. However, because of the use of impure argon containing O_2 these half-lives for sample C are only lower limits.) The half-life for a new sample solution was always found to be too short, presumably due to O_2 still present despite the purifications used, and the final equilibrium half-life is not reached until many hours after the run is started—at 373°K. about 1800 hours were necessary as shown in Fig. 6.

With the M, O, Q and R samples results were obtained at several different temperatures as given in Table III and plotted in Fig. 2. Where several half-life determinations were averaged together, the error quoted is the average deviation, and the number in parentheses is the number of determinations which were averaged together. The half-life at 408°K. for the M series is a lower limit since the half-life was still increasing at this temperature when the series of runs was discontinued. After the results reported for the O sample were obtained, the solution was buffered with a HSO_3^-–$SO_3^=$ buffer, and the half-life decreased by a factor of 100 and was relatively constant for several runs. This probably indicates that HSO_3^- is too powerful an oxidizing agent for use with alanine solutions although HSO_4^- apparently does not decompose alanine. At the higher temperatures (391 to 427°K.) (Q and R series) a gradual increase of the half-life to a maximum similar to that observed at 373°K. was observed. Only the half-lives on the horizontal portion of the curves were averaged and recorded in Table III.

The data recorded in this table were collected in the order across and down, in general. Since it seems reasonable that the half-lives determined last should be closest to the true oxidation free half-lives, the last row of half-lives for the Q series and the average of the last two rows of half-lives for the R series are plotted in Fig. 2.

The room temperature half-lives (J, Q and R series) were less than or of about the same value as the values for 47 and 69° given in Table III. The relation between the observed half-life, $t_{1/2\text{o}}$, the low temperature half-life, $t_{1/2\text{e}}$, and the half-life for the true thermal decarboxylation reaction, $t_{1/2}$, should be given by eq. 7

$$\frac{1}{t_{1/2\text{o}}} = \frac{1}{t_{1/2\text{e}}} + \frac{1}{t_{1/2}} \qquad (7)$$

From the values of $t_{1/2\text{o}}$ in Table III from 357–391°K. and the $t_{1/2\text{e}}$ value for the R series, the true decarboxylation half-lives were calculated from eq. 7. The results are given as the crosses in Fig. 2, with an uncertainty of 50% in the largest half-life. The straight line drawn in Fig. 2 through the decarboxylation half-lives for the higher temperatures, 373 to 427°K., where the rates are only slightly affected by the limiting rate observed at room temperature, gives an Arrhenius activation energy of 38.6 ± 1.0 kcal./mole where the error was estimated from the largest and smallest slope possible through the four points. This activation energy gives the final expression for the thermal decarboxylation half-life, independent of extraneous effects such as oxidation and radiation damage due to labelling radiocarbon. It is

$$\underset{\text{(years)}}{t_{1/2}} = 1000e^{-38600/1.986(1/396 - 1/T)}$$

This gives the room temperature (25°) half-life relative to decarboxylation (oxidation would of course shorten this life, as would other destruction mechanisms such as bacterial attack) to be 10 billion years.

Exchange Reaction.—Many runs were made in the absence of carrier CO_2 from 373 to 427°K., *e.g.*, at 373°K. in the aqueous R series consecutive rates of 0.332, 0.369, 0.324, 0.379 and 0.363 were determined where the last run was in the absence of carrier CO_2. The results all showed that there was no observable bimolecular exchange reaction since the rate was experimentally independent of the CO_2 pressure.

Heterogeneous Effect.—If the alanine were to be weakly absorbed on the Pyrex surface so that the concentration of alanine on the wall were proportional to that in the solution, the heterogeneous half-life should be inversely proportional to the surface to volume ratio, but, if it be strongly absorbed, this half-life should be inversely proportional to the total amount of surface and directly proportional to the total amount of carrier alanine since the entire surface would be covered with a monolayer of alanine. If any heterogeneous effect were due to the removal of some active component from the wall into the solution followed by its rapid reaction with alanine, the half-life would follow the same law as with the second assumption. In the case of the first assumption the half-life for the expected reaction in the S series for which the glass area was increased 210-fold should have been 50 years at 373°K. if the P reaction were entirely heterogeneous; for the second assumption it would be 1.5 years. The results are given in Fig. 6. Apparently there is an observable heterogeneous effect at 373°K. although it is not of the magnitude expected for any set of assumptions for the heterogeneous mechanism. This could mean that the 373°K. reactions (except for the S series) are only partially heterogeneous, but a more plausible mechanism is that the surface increases the chain length of the radiation induced reaction. Heating the glass to about 408°K. for 164 hours apparently decreases the magnitude of the heterogeneous effect (S results after the break in the curve at 2400 hours).

Radiation Induced Reaction.—The average energy of the C^{14} β is 0.045 Mev.[6] The G factors for radiation damage by 50 kev. X-rays at room temperature in 1 M O_2-free alanine solutions were determined as 1.92 molecules of pyruvic acid and 0.59 molecule of CO_2 per 100 e.v.[12] The pyruvic acid probably does not decarboxylate below 373°K. and certainly not at room temperature. Therefore, since the other "tagged" radiation damage product, propionic acid, is stable and very soluble, the total G factor for our application is that for CO_2 alone—0.59. By the use of eq. 5 the expected half-lives for the radiation damage reaction at 298°K., $t_{1/2\text{r}}$, were calculated and compared in Table IV with the experimental values for the half-life at this temperature, $t_{1/2,\text{o}}$, for the three results.

TABLE IV

COMPARISON OF THE EXPERIMENTAL HALF-LIVES AND THE EXPECTED RADIATION DAMAGE HALF-LIVES AT 298°K.

Sample	$A \times 10^{-7}$, d.p.m.	$n \times 10^{2}$, moles	$t_{1/2\text{r}} \times 10^{-5}$, yr.	$t_{1/2\text{o}} \times 10^{-5}$, yr.
J	2.14	0.131	1.83	0.58
Q	7.85	1.20	4.56	0.64
R	7.85	3.41	12.9	1.2 ± 0.5

The Q half-life is not very reliable because of the small amount of C^*O_2, 2.2 dpm. If the pyruvic acid were to decarboxylate under the experimental conditions, $t_{1/2\text{r}}$ would be 24% of those listed. The effect of the buffer on the G values is unknown. In view of the agreement between the calculated and observed rates, there seems to be little doubt that the radiation effect was mainly responsible for the observed rates at low temperatures.

Discussion

Mechanism of the Decarboxylation Reaction.—It is seen from Fig. 2 that the half-lives for the reaction in the solutions were 3 to 10 times Abelson's extrapolated values,[7] and also that the activation energy of 38.6 kcal./mole is reasonably close to the value of 41 kcal./mole obtained by Abelson for aqueous solutions at much higher pressures. The half-lives for decarboxylation in the solid phase are also approximately the same as in the aqueous phase as found by Abelson for alanine ground up in a $CaCO_3$ matrix. Therefore, the decarboxylation reaction observed by Abelson was observed in these experiments down to about 373°K.

The various aqueous samples differed in the concentrations of ions and ionic strength, μ. In order to calculate the molalities of the ions, the concentration equilibrium constant for reaction 8, K'

$$HSO_4^- = SO_4^{=} + H^+ \qquad (8)$$

and that for reaction 9, K''

$$RH^+ + R^{\pm} + H^+ \qquad (9)$$

are required where RH^+ is $CH_3CH(NH_3^+)CO_2H$ and $R^{\pm}$ is $CH_3CH(NH_3^+)CO_2^-$. The activity equilibrium constant for (8) is 1.14×10^{-4} [13] and that for (9) is 2.14×10^{-3} [14] at 427°K. The activity coefficient ratio, $\gamma_{H^+} \cdot \gamma_{SO_4^-} / \gamma_{HSO_4^-}$, at 427°K. and at various ionic strengths was estimated from the work of Maranville[15] on the Raman spectra of NH_4HSO_4 solutions at 0, 25 and 50°. The analogous ratio for equilibrium 9 was estimated from the work of Batchelder and Schmidt[16] by an extrapolation of their curves from a μ of 2.9 to 5.8. It was assumed that this latter ratio is constant with temperature which is a fairly good assumption for uni-univalent ion pairs. From these quantities the values of K' and K'' were estimated.

By the use of the two concentration equilibrium constants, K' and K'', and the total molalities for the alanine and HSO_4^-–$SO_4^{=}$, the molalities of the various ionic species, (X), were calculated by the method of successive approximations. It can be shown that 100% of the alanine in unbuffered solutions is present as the zwitterion even at 427°K. in the manner of Edsall and Blanchard.[17] It was assumed that the alanine present as the zwitterion is

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TABLE V

MOLALITIES AND IONIC STRENGTHS OF THE AQUEOUS SOLUTIONS AT 427°K.

Sample	$K' \times 10^2$	$K'' \times 10^3$	(RH^+)	$(R^{\pm})$	(Na^+)	(HSO_4^-)	$(SO_4^=)$	$\frac{(R^{\pm})}{(R^{\pm}) + (RH^+)}$	$(\mu)^{1/2}$
M	0.96	1.1	0.141	0.029	1.42	0.34	0.61	0.17	1.48
O				.78				1.00	0.88
Q	2.9	0.60	.84	.26	2.80	.12	1.76	0.24	2.38
R	1.6	0.88	.58	.97	1.27	.03	0.91	0.63	1.93

the same as NaCl in calculating the ionic strengths listed in Table V.

The predominant molecular species present in solid alanine is the zwitterion which explains the fact that the melting point for alanine is greater than 297°. Considering the ionic species present in solution and in the solid phase and the fact that the first-order alanine decarboxylation reaction has about the same half-life in the presence as in the absence of water, there are two possible rate-determining steps for the decarboxylation reaction

$$R^{\pm} \longrightarrow CH_3\text{-}CHNH_3^+ + CO_2 \qquad (10)$$

and

$$RH^{\pm} \longrightarrow CH_3\text{-}CHNH_3^+ + CO_2 + H^+ \quad (11)$$

both of which would be followed by the fast step

$$CH_3\text{-}CHNH_3^+ + XH \longrightarrow CH_3CH_2NH_3^+ + X^- \qquad (12)$$

where XH is HOH or $R^{\pm}$.

Since the heat of ionization of RH^+ is about 0.74 kcal./mole,[18] reactions 10 and 11 have about the same change in enthalpy so the heat of activation for (11) could be equal to that for (10) even though an additional bond must be broken in (11). However, the entropy of activation for the formation of a solvated proton and a negative residue is about −15 to −25 e.u.,[19] so reaction 11 should have a steric factor at least 10^{-3} smaller than reaction (10). Also, there would be a much greater dependence of the half-life upon the ionic strength than is shown by comparing the half-lives in Table III to the ionic strengths in Table V if reaction 11 were involved in the mechanism.[20] In addition, if reaction 10 were the only mechanism for decarboxylation, the mechanism would be analogous to that found by Verhoek[21] and others for the trihaloacetic acids. The experiments in this Laboratory were not performed at sufficiently low *p*H's to determine whether the mechanism involves (10) or the assumed (10) and (11) combination. If (10) be the only mechanism, the half-lives quoted from about 373 to 427°K. must be multiplied by the factor $(R^{\pm})/[(R^{\pm}) + (RH^+)]$ (Table V for the 427°K. quantities) to obtain the true half-life for this species.

The Oxidation Reaction.—By the use of the experimental half-life for the oxidation reaction at 373°K. of 4.5 years determined with the J sample and the approximate Arrhenius activation energy for the oxidation reaction of 25 kcal./mole determined by runs with impure argon (results not tabulated), the half-life at room temperature for the oxidation reaction is estimated to be about 20,000 years.

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CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO]

Halides as Bridging Groups for Electron Transfer in the Systems $Cr^{++} + (NH_3)_5CrX^{++}$

BY ALLEN E. OGARD AND HENRY TAUBE

RECEIVED AUGUST 19, 1957

The spontaneous reaction of the ions $(NH_3)_5CrX^{++}$ in acid solution leads to $(NH_3)_5CrOH_2^{+++} + X^-$ as products, but when Cr^{++} is present, reaction to form CrX^{++} and NH_4^+ takes place. The rate law for the Cr^{++} catalyzed dissociation of $(NH_3)_5CrCl^{++}$ has been established by a detailed kinetic study. The rate is proportional to the concentration of $(NH_3)_5$-$CrCl^{++}$ and of Cr^{++} and is independent of the concentrations of H^+, $CrCl^{++}$ and of Cl^- at least at moderate concentrations. The second-order specific rate at 25° and $\mu = 1$ for X = F, Cl, Br and I are 0.016, 3.08, 19.4 and 330 ± 100 l. mole^{-1} min.$^{-1}$, respectively; the enthalpies of activation for the first three are 13.4, 11.1 and 8.5 kcal. mole^{-1}, respectively. The change in solvent from H_2O to 86% D_2O–14% H_2O for the reaction $Cr^{++} + (NH_3)_5CrCl^{++}$ causes a decrease in rate by a factor of 0.77.

A central point of interest in the subject of oxidation–reduction reactions of metal ions is the specific influence exerted on the rates of reaction by negative ions and other groups, and the mechanisms by which these influences are exerted. These influences are particularly interesting when the catalytic groups are not readily oxidized or reduced by the metal ions. Careful measurements of the effect of halide ions and hydroxide ion on the rate of the "electron exchange"[1] between Fe^{++} and Fe^{+++} have been made,[2,3] and rate coefficients

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[1] Used here without implication of mechanism, to describe oxidation–reduction systems in which no net chemical change takes place.

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