$\Delta E + RT\,\Delta n$. In addition by using published heat capacity data[12] and Kopp's rule for MoO_2, a change is made to the customary standard temperature. There then result the equations

$$Mo(c) + 3/2O_2(g.\ 298.16\,^\circ K.,\ \text{unit fugacity}) = MoO_3(c)$$
$$\Delta H = -744.65 \pm 0.40 \text{ int. kjoules}$$

$$MoO_2(c) + 1/2O_2(g.\ 298.16\,^\circ K.,\ \text{unit fugacity} = MoO_3(c)$$
$$\Delta H = -155.30 \pm 0.127 \text{ int. kjoules}$$

By combining these reactions properly, there is obtained

$$Mo(c) + O_2(g.\ 298.16\,^\circ K.,\ \text{unit fugacity}) = MoO_2(c)$$
$$\Delta H = -589.36 \pm 0.53 \text{ int. kjoules}$$

The uncertainties are obtained from the square root of the sum of the squares of the precision error assigned to the combustion value, the calibration value, and the benzoic acid heat value. That for the last reaction, above, is obtained by summing the extremes of the first two reactions.

PITTSBURGH, PA.

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(12) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SASKATCHEWAN]

Chemical Effects of the $C^{12}(\gamma,n)C^{11}$ Reaction in Anhydrous Sodium Carbonate[1]

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When sodium carbonate crystals, which have been exposed to γ-radiation from a betatron operating at a peak energy of 23 Mev., are dissolved in water, C^{11} is found to be present in carbonate, carbon monoxide, formic acid, oxalic acid, glyoxylic acid and glycolic acid. The distribution of C^{11} activity between these compounds has been measured, and found to be independent of twofold variations in the total γ-ray dose or in the dose rate. The distribution is also independent of the *p*H of the solution in which the crystals are dissolved. The distribution of the C^{11} activity between the two positions of the glyoxylic and glycolic acid molecule has been determined. If the crystals are heated at a series of increasing temperatures before dissolving, the percentage of the C^{11} present as glyoxylic acid, glycolic acid and oxalic acid decreases, each at a different temperature, and the corresponding activity appears instead as carbonate. A mechanism is suggested to account for the experimental results.

Introduction

Only a few studies of the chemical effects following the (γ,n) nuclear reaction have been reported. In particular, Rowland and Libby[3] have studied the distribution of C^{11} between carbon monoxide and carbon dioxide following the irradiation of solid and liquid carbon dioxide, solid sodium bicarbonate and solutions of sodium bicarbonate and sodium carbonate in water, using γ-rays from a betatron operating at a maximum energy of 48 Mev. It was found that the irradiation of samples in the solid phase yielded about 50% of the radioactive atoms in each oxide, while the irradiation of samples in the liquid phase yielded 95–100% of the radioactivity in the form of carbon monoxide.

This work reports the results of an investigation of the $C^{12}(\gamma,\ n)C^{11}$ reaction in anhydrous sodium carbonate. The recoil energy of the resulting C^{11} nucleus arises from the momentum of the incident γ-ray as well as from the recoil due to the emitted neutron. For a 24 Mev. γ-ray, these energies are approximately 1500 e.v. and a maximum of 0.5 Mev., respectively, the latter figure assuming that all the energy of the γ-ray in excess of the threshold energy for the (γ,n) reaction appears as kinetic energy of the product particles. The recoiling carbon atom will almost certainly be ionized initially, but as it is slowed down through collisions, partial or complete neutralization will soon occur. As the recoiling atom loses energy it may also react with atoms or molecules to form unstable combinations which may later undergo further reactions. When thermal energies are attained, the carbon atom may be combined in the form of a stable molecule or a radical which can react with the solvent when the crystals are dissolved. Some information concerning these processes can be obtained by investigating the chemical forms in which the C^{11} appears in the solution of the irradiated crystals.

Experimental

Two samples of sodium carbonate were prepared by heating reagent grade sodium carbonate and reagent grade sodium bicarbonate to constant weight at 300°. These samples were stored in a desiccator over P_2O_5 until used.

For irradiation, samples of sodium carbonate were placed in sealed lucite capsules and exposed to radiation from the University of Saskatchewan betatron operating at a maximum energy of 24 Mev. The intensity at the position of irradiation varied from approximately 1000 to 2000 roentgens per minute in different experiments. The irradiation time was either 10 or 20 minutes.

Decay measurements on irradiated samples indicated the formation of O^{15} ($t_{1/2}$ = 126 seconds), C^{11} ($t_{1/2}$ = 20.6 minutes) and a small amount of Na^{24} ($t_{1/2}$ = 14.8 hours), the latter presumably due to stray neutrons. The total C^{11} activity produced in each irradiation was determined by counting a weighed amount of the sample with a mica-window end-on counter. Measurements were made at least 30 minutes after irradiation to permit decay of the short lived O^{15} activity. Corrections were made for the small amount of Na^{24} activity. An empirical calibration curve was used to correct for different weights of material counted.

To investigate the gaseous compounds which might contain C^{11} activity, 0.5 g. of irradiated sodium carbonate was dissolved in 10 ml. of water in a flask connected to a gas analysis train. A stream of air containing known amounts of carbon monoxide and methane as carrier gases was bubbled slowly through the solution as it was acidified. The gases passed through a sodium hydroxide solution to absorb the liberated carbon dioxide, then over hot copper oxide at 500° to oxidize carbon monoxide to carbon dioxide which was in turn absorbed in sodium hydroxide solution. The remaining gases were then passed over copper oxide at 800°, where methane was oxidized to carbon dioxide. This also was absorbed in sodium hydroxide solution. The carbonate

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(1) Abstracted from a thesis presented by L. J. Sharman in partial fulfillment of the requirements for the degree of Ph.D. in Chemistry from the University of Saskatchewan.

(2) Holder of a C.I.L. Fellowship, 1952–1953.

(3) F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1493 (1953).

fractions were precipitated as barium carbonate, which was washed, dried and counted for C^{11} activity. In one experiment, acetylene was used as the carrier gas. This was absorbed in an alkaline bromine solution and counted with a solution counter.

The percentages of the total C^{11} activity which were found present as carbon dioxide and carbon monoxide are given in Table I. The activity present in the methane and acetylene carriers was found to be zero within experimental error.

TABLE I

COMPOUNDS CONTAINING C^{11} ACTIVITY WHEN IRRADIATED Na_2CO_3 CRYSTALS ARE DISSOLVED IN WATER

Compound	% of the total C^{11} activity	Compound	% of the total C^{11} activity
Carbon dioxide	22 ± 1	Oxalic acid	39 ± 1
Carbon monoxide	1 ± 1	Glyoxylic acid	24 ± 1
Formic acid	3 ± 1	Glycolic acid	10 ± 2

To investigate non-gaseous compounds containing C^{11} which were formed on solution of the irradiated solid, one gram of the sodium carbonate was dissolved in 10 ml. of water containing the desired carriers, and the solution was acidified. The use of formaldehyde carrier, which was precipitated as the 2,4-dinitrophenylhydrazone derivative, indicated that considerable activity was carried. However, on repeated recrystallization the specific activity was reduced to zero, indicating that formaldehyde was not one of the products of the reaction. Radioactive methanol was shown to be absent by use of methanol carrier, distillation of the solution, and oxidation of the methanol in the distillate to formaldehyde with $KMnO_4$ and H_3PO_4. The formaldehyde produced was precipitated as the 2,4-dinitrophenylhydrazone derivative, which was found to be inactive. Other preliminary tests showed that C^{11} activity did follow formic acid, oxalic acid, glyoxylic acid and glycolic acid carriers. The procedures used to separate these carriers from an acidified solution of irradiated sodium carbonate and to determine the percentage of the total C^{11} activity present in each fraction are outlined below.

Formic Acid.—The glyoxylic acid carrier was precipitated as the 2,4-dinitrophenylhydrazone derivative. The solution was then distilled. The formic acid contained in the distillate was oxidized with mercuric chloride to carbon dioxide, which was absorbed in sodium hydroxide solution. The carbonate was then precipitated as barium carbonate, washed, dried, weighed and counted.

Oxalic Acid.—The solution of the irradiated sodium carbonate and carriers was acidified with acetic acid. Calcium oxalate was precipitated, washed, dissolved in dilute hydrochloric acid and reprecipitated by the addition of aqueous ammonia. The reprecipitation procedure was repeated until a constant specific activity was obtained.

Glyoxylic Acid.—The glyoxylic acid was precipitated from the acidified solution as the 2,4-dinitrophenylhydrazone derivative. For purification, the derivative was dissolved in ethyl acetate, and then extracted from the ethyl acetate into a saturated sodium bicarbonate solution. The derivative was then reprecipitated by acidification of the solution. This procedure was repeated until a constant specific activity was obtained.

Glycolic Acid.—From the acidified solution containing carriers, glyoxylic acid was precipitated as the 2,4-dinitrophenylhydrazone derivative. To remove the last traces of active glyoxylic acid, further portions of glyoxylic acid carrier were added to the filtrate and precipitated as before. The oxalate activity was removed by neutralization and precipitation as the calcium salt. Traces of oxalate activity still remaining in the solution were removed by the addition of a small amount of sodium oxalate and precipitation as calcium oxalate. The solution was then made strongly basic with sodium hydroxide. After centrifugation, potassium permanganate was added to the filtrate and the solution was heated to oxidize glycolate to oxalate. The excess permanganate was then reduced with formaldehyde and the precipitate of manganese dioxide was removed. The resulting clear solution was acidified with acetic acid and the oxalate was precipitated as the calcium salt. The specific activity of the precipitate was found to be independent of the yield in the oxidation reaction.

Radioactive glyoxal was shown to be absent by an experiment in which glyoxal carrier was included with the others in the solution of the irradiated sodium carbonate. After acidification, the 2,4-dinitrophenylhydrazones of glyoxylic acid and glyoxal were precipitated together. The two derivatives were separated by repeated boiling with 95% ethanol, in which the glyoxylic acid derivative was soluble, while the glyoxal derivative was almost insoluble. The glyoxal derivative was further purified by recrystallization from nitrobenzene and was found to be inactive.

Results

The percentages of the total C^{11} activity present in the different fractions are shown in Table I. Each result is the average of several determinations. The reported uncertainties are due to the standard deviations in the counting, an estimate of the uncertainties in the correction curve for the weight of sample counted, and the uncertainty in the experimental determination of the fraction of the added carriers which was recovered.

Similar determinations were made on crystals which had been irradiated for ten minutes with the betatron operating at a peak energy of 23 Mev., followed by irradiation for 15 minutes at a peak energy of 15 Mev. (below the threshold energy). The roentgen dose below threshold was about two-thirds of that above threshold. The results showed that exposure to this additional γ-ray dosage did not produce any change in the relative amounts of the compounds produced within the uncertainties given in Table I. Variation of a factor of two in the dose rate at constant total dose, or in the total dose at constant dose rate, did not produce any change in the distribution of C^{11} activity within these same limits.

The results given in the table were also found to be the same for both of the sodium carbonate samples which were prepared, and to be the same if the irradiated sample was dissolved in solutions of *p*H zero, seven or fourteen.

Solutions prepared by dissolving irradiated sodium carbonate in distilled water were tested for the presence of hydrogen peroxide, formic acid, formaldehyde, oxalic acid, glyoxylic acid and glycolic acid by spot tests which were capable of detecting 5×10^{-5} mole of substance per mole of irradiated sodium carbonate. The tests in each case were negative.

Distribution of C^{11} Activity between the Two Carbons of Glyoxylic Acid and of Glycolic Acid.—Since the molecules of these acids are unsymmetrical it was possible to determine the distribution of C^{11} activity between the two carbon atoms of the molecule.

Glyoxylic acid was decarboxylated by heating the 2,4-dinitrophenylhydrazone derivative at 205° in a stream of nitrogen. The evolved carbon dioxide was absorbed in NaOH solution and precipitated as $BaCO_3$. It was found that 24 ± 2% of the C^{11} activity present in the glyoxylic acid was located in the carboxyl position. This percentage was not altered when the irradiated sodium carbonate crystals were exposed to betatron radiation with a peak energy of 15 Mev., suggesting that the appearance of activity in both positions of the molecule was not due to some exchange reaction in the crystal brought about by the ionization from the γ-rays.

The distribution of C^{11} activity between the two positions of glycolic acid was determined by oxidation with periodic acid. This causes oxidation of the alcohol group to formaldehyde while the carbon from the carboxyl group appears as carbon dioxide. An aqueous solution of irradiated sodium carbonate was prepared containing carriers for the active substances present. The solution was brought to pH 7 with sulfuric acid and excess periodic acid was added. When the solution was distilled, formaldehyde appeared in the distillate. This was precipitated as the 2,4-dinitrophenylhydrazone derivative. Activity measurements on the precipitate indicated that 10 ± 7% of the C^{11} activity present in the glycolic acid was present in the alcohol group.

Effect of Heat Treatment of Irradiated Crystals.—The irradiated samples of sodium carbonate were heated for ten minutes in a muffle furnace at selected temperatures from 140 to 800°. For these experiments, the total C^{11} activity was measured on an unheated portion of the sample. Preliminary tests carried out at 800° indicated that less than 2% of the C^{11} activity was lost by the heat treatment, and that the loss in weight was less than 1%.

The heated samples were dissolved in water and the distribution of C^{11} activity between carbon monoxide, carbon dioxide, oxalic acid, glyoxylic acid and glycolic acid was determined. The activity in the carbon monoxide fraction remained unchanged at 1 ± 1%. The results for the other compounds after heat treatment at various temperatures are shown in Fig. 1. This shows that around 140° the amount of radioactive glyoxylic acid begins to decrease, radioactive glycolic acid around 340° and radioactive oxalic acid around 400°. In each case the corresponding C^{11} activity appears in the carbonate fraction. After heating at temperatures of 500° and above, essentially all of the C^{11} activity is in the form of carbonate, except for 1 ± 1% which appears as carbon monoxide.

The distribution of C^{11} activity between the two positions of glyoxylic acid was determined on a sample which had been heated at 145° for ten minutes before dissolving. This treatment reduced the percentage of the total C^{11} activity appearing in the glyoxylic acid fraction from 24 ± 1% to 19 ± 2%. It was found, however, that of the activity appearing in glyoxylic acid, the percentage present in the carboxyl group was unchanged at 24 ± 2%. Further experiments showed that an irradiation for 15 minutes at 15 Mev. following the ten-minute irradiation at 23 Mev. also produced no change in the relative amounts of C^{11} appearing in the two positions of glyoxylic acid.

Discussion

Some of the compounds produced when the irradiated sodium carbonate was dissolved in water, contain hydrogen, in particular glyoxylic acid and glycolic acid. It is very unlikely that these compounds are present as such in the irradiated crystals. The sodium carbonate used in these experiments was stored over P$_2$O$_5$ and the loss in weight of the material when dried at 275° was less than 0.01%. The probability is very small that a sufficient number of water molecules to furnish the hydrogen required for these compounds would be available in the vicinity of a recoiling carbon atom in the crystal. It appears more likely that the compounds are produced when reactive fragments or radicals trapped in the crystal react with water as the material is dissolved.

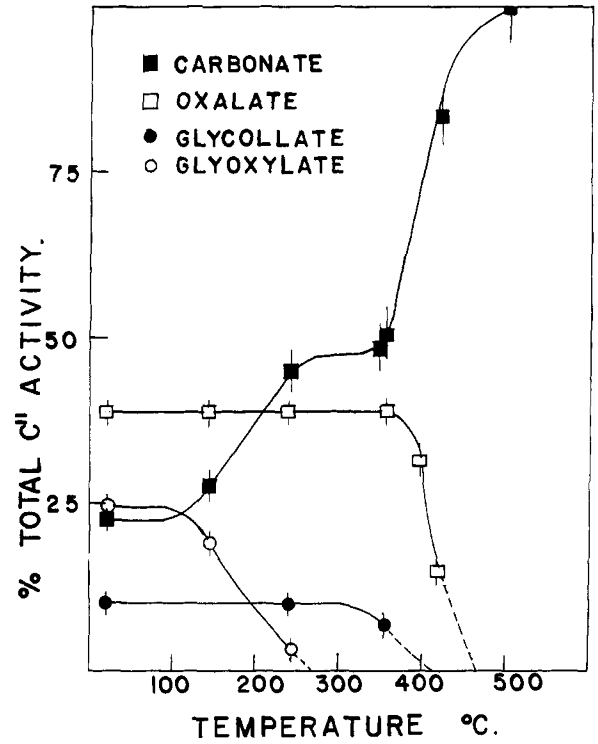


Fig. 1.—Effect of a ten minute heat treatment at different temperatures upon the distribution of C^{11} activity.

The results of the heating experiments shown in Fig. 1 indicate that oxalic acid, glyoxylic acid, and glycolic acid do not all originate from a single type of radical in the crystal, which can react with water by competing reactions to form these different compounds. In this case, one would expect a simultaneous decrease in all three of these compounds if the radical was destroyed by heating. Instead, the results indicate that there exist in the crystal separate radicals for the formation of each of these compounds, the radical or radicals leading to each compound being destroyed at different temperatures under the conditions of the heating experiments. The effect of the heating in each case is to change the radicals leading to these compounds to a species which yields carbonate ion in solution.

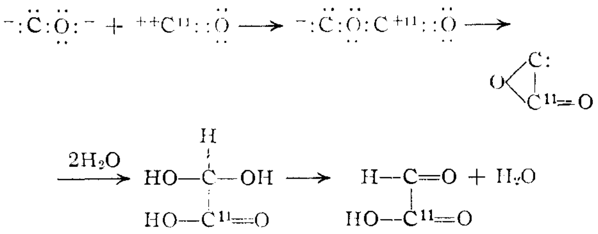
It appears possible that there are at least two different radicals which yield glyoxylic acid when the crystals are dissolved, corresponding to the formation of glyoxylic acid labeled with C^{11} in either the carboxyl or the aldehyde group. From the effect of the heating on the total amount of glyoxylic acid and the distribution of C^{11} activity between the two groups, the ratio of the rates of destruction of the two radicals would be 1 ± 0.2. It is also conceivable that the two forms of glyoxylic acid are produced as the result of two competing reactions between a single radical and water. Similar considerations may hold for glycolic acid.

A significant result of the heating experiments is that when the amount of C^{11} appearing in one compound is decreased by heating, the activity appears instead in the form of carbonate. This corresponds formally to an oxidation. The oxidation does not appear to proceed in a stepwise fashion, since then, for example, the amount of radioactive oxalate should increase as the amount of radioactive glyoxylic acid decreases. The oxidation of one species to another corresponds to the loss of electrons, but it is unlikely that this is the mechanism, since the oxidation of the radical leading to glycolic acid would require the loss of six electrons during the heating process. Oxidation of the radicals by the carbonate ions in the crystal is considered to be unlikely. A more likely possibility is that the radioactive species is oxidized by reactions with atoms or radicals which the recoiling C^{11} had produced by collisions in the crystal. Under the influence of heat these radicals could diffuse to the radioactive species and cause oxidation. To account for the complete oxidation to carbonate, it is necessary that a sufficient number of oxidizing atoms or radicals be located in close proximity to the radioactive species. The local heating produced by the reaction with one of these could supply the necessary activation energy to complete the oxidation to the carbonate form.

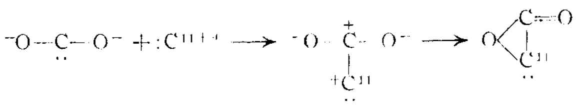
The following simplified mechanism is suggested to explain the experimental results. The recoiling carbon fragment contains carbon in the 4+ oxidation state, *e.g.*, $C^{11}O^{++}$ or $C^{11}O_2$, when its energy is lowered to the value at which it is able to form the radioactive species giving rise to the observed compounds. This fragment may collide with a carbonate ion in the crystal. If the kinetic energy is not too high, the excess kinetic energy may be lost, leaving the fragment with thermal energy. However, if the fragment has sufficient energy, it could react with the carbonate ion to form a two-carbon radical, with the loss of a certain number of oxygen atoms, the number depending upon the kinetic energy at the time of collision. The oxygen atoms lost could be either from the carbonate ion or from the recoiling radioactive fragment. On heating, the oxygen atoms may recombine with the radical, resulting in oxidation to the 4+ oxidation state. If the crystal is dissolved in water, H_3O^+, OH^- or H_2O could add to the radical to form the observed compounds, assuming that no oxidation or reduction reactions occur at this stage.

The loss of zero, one, two or three oxygen atoms on collision would give rise to radicals yielding carbonate (22%), oxalate (or formate + carbonate) (42%), glyoxylate (24%) or glycolate (10%), respectively. On the basis of this hypothesis, it appears that the most probable energy for the recoiling fragment at the stage where it forms these radicals is that which is sufficient for combination with carbonate with the loss of one oxygen atom.

The loss of oxygen from the recoiling fragment rather than the carbonate ion leads to the possibility of the formation of different radicals with the same over-all oxidation state. Hypothetical structures can be written for the resulting radicals. For example, glyoxylic acid results from the radical produced when two oxygen atoms are lost. If it is assumed that the recoiling C^{11} at this stage is in the form of $C^{11}O^{++}$, and that the two oxygen atoms are lost from the carbonate ion, leaving a $CO^{=}$ species, carboxyl-labeled glyoxylic acid could result from the mechanism



If instead, $C^{11}O^{++}$ and $CO_3^{=}$ each lose one oxygen atom in the collision process, the production of a radical identical except for the position of the C^{11} atom results.



This could react with water to produce aldehyde-labeled glyoxylic acid. The identity of the two radicals is consistent with the experimental observation that the two forms of glyoxylic acid disappear at about the same rate when heated.

Similar mechanisms can be written for the formation of the other observed compounds, but the validity of these detailed processes is doubtful.

The effect, if any, of the ionization produced by the betatron beam upon the processes leading to the formation of the observed radioactive compounds is not known. If any such effect does exist, an equilibrium state must have been reached in the experiments reported here, since ionization produced by exposure to radiations with energy below the threshold value for the formation of C^{11}, after an initial exposure to high energy γ-rays, produced no further change in any of the measured quantities. The results were also not changed by variations by a factor of two in the total dose or the dose rate. The results obtained do not indicate that ionization effects are playing any important role in the processes governing the fate of the C^{11} atoms produced by the (γ, n) reaction in sodium carbonate.

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SASKATOON, CANADA