

C13 Isotope Effect in the Decarboxylation of Malonic Acid

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THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few half-tone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$4.00 per page) will not be made and no reprints will be furnished free.

Anomalous Negative Peaks in Mass Spectra

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August 15, 1949

IN the mass spectra of the gases O_2 , N_2 , CO , and CO_2 , negative peaks have been found approximately two mass units lower than the peaks of the positive molecular ions. Arnot¹ and Sloane and Press,² using mass spectrometer tubes of special design, observed negative peaks corresponding roughly in mass to positive ions of these same gases. For the present work a conventional spectrometer was used (Consolidated Model 21-102).

The mechanism for negative ion formation that seems most probable is that proposed by Arnot¹ and Arnot and Beckett.³ In this process, the positive ion captures an electron at the metal surface and is neutralized but left excited. This is followed by either: (1) capture of another electron forming a negative ion of the same type, or (2) transfer of the energy of the positive ion to another type atom on the surface, which in turn captures an electron forming a negative ion of another type.

Negative peaks have been observed with various ion sources while using the same analyzer section of the mass spectrometer tube. This indicates that the source of the negative peaks is in the region of the exit slit of the analyzer section and probably arises from a non-conducting layer on the exit slit plate. A schematic diagram of this possible source of negative ions from carbon monoxide is given in Fig. 1. With field conditions set to focus positive ions of mass 26, mass 28 ions will have a larger radius and strike some point (as shown) on the exit slit plate. This spot on the plate will then act as the source of negative ions, which are deflected by the magnetic field, collected, and recorded as a negative peak at 26.2 on the mass scale. The difference in radius of the "mass 26.2" and mass 28 ions is approximately two millimeters. Assuming that the negative ions CO^- are formed with very low energy, the radius of the path of these ions would be about this value, making it possible for them to be collected. In Fig. 2 is shown a negative peak near mass 26.2 on a portion of a CO spectrum.

Table I gives the ratio of negative to positive ions for the gases studied thus far. These values are of the same order of magnitude as the probabilities of conversion given by Arnot¹ for O_2 , 0.42×10^{-4} , and CO_2 , 2.3×10^{-4} .

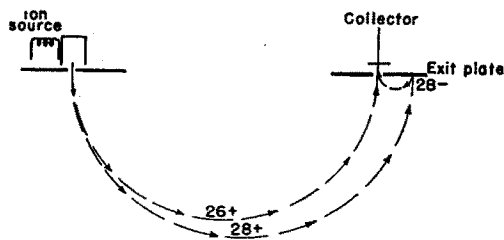


FIG. 1. Possible source of negative peaks.

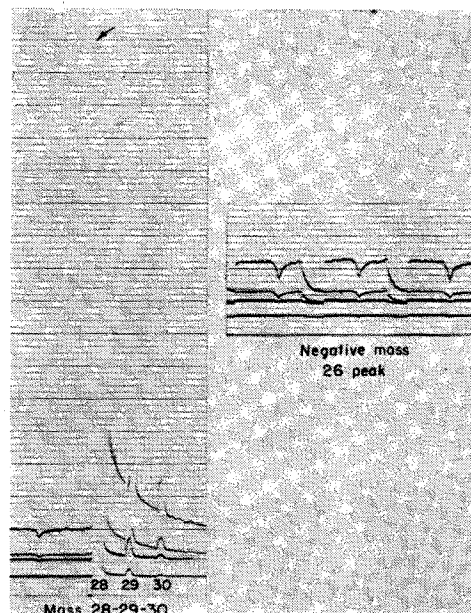


FIG. 2. Portion of CO spectrum.

TABLE I. Ratio of negative to positive ion peaks for various gases.

N_2	2.9×10^{-4}
O_2	3.5×10^{-4}
CO	4.5×10^{-4}
CO_2	5.9×10^{-4}

The negative ion N_2^- is known to be unstable and was not detected by Arnot,¹ but in the present work on N_2 a negative peak near 26.2 was found. This may be due to a negative ion of another type, according to Arnot's mechanism (2) (see above). However, the detection of N_2^- is feasible in the present case because of the short distance traversed to the collector. Further, negative peaks in the spectra of all four gases appear to have the same shape. If a transfer of energy were involved, the ions formed would possibly have a large energy spread giving broad peaks. Therefore, the negative peak in the spectrum of N_2 is probably due to N_2^- .

It was difficult to obtain an accurate peak height vs. pressure relationship because of the size of the peak; however, as nearly as could be determined, this relationship was linear up to three times normal operating pressure. Any negative ions from hydrocarbons formed by this process would not be detected because of the much larger positive ion peaks occurring at the same masses.

We would like to express our appreciation to Dr. J. A. Hipple for his helpful discussion concerning a possible source of the negative ions.

¹ F. L. Arnot, Proc. Roy. Soc. (London) **A158**, 137-156 (1937).

² R. H. Sloane and R. Press, Proc. Roy. Soc. (London) **A168**, 284-301 (1938).

³ F. L. Arnot and C. Beckett, Proc. Roy. Soc. (London) **A168**, 103-122 (1938).

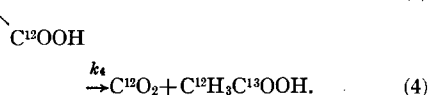
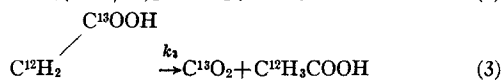
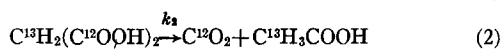
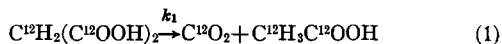
C^{13} Isotope Effect in the Decarboxylation of Malonic Acid

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August 17, 1949

IN a recent publication by one of us,¹ a theoretical treatment of the C^{14} isotope effect in the decarboxylation of malonic acid was given. The results of the theory are in sharp disagreement with the experiments of Yankwich and Calvin.² The recent experiments

of Lindsay, McElcheran, and Thode³ on the C^{13} isotope effect in the decomposition of oxalic acid into CO_2 , CO , and H_2O are of the order of magnitude predicted for malonic acid. The isotope effects should be comparable in the decarboxylation of oxalic and malonic acids. We have studied the isotope effect in the decarboxylation of malonic acid by following the isotopic composition of the CO_2 liberated from ordinary malonic acid.

The decomposition of malonic acid gives $C^{13}O_2$ and $C^{12}O_2$ according to the following equations



Since the reaction is first order, the ratio $C^{13}O_2/C^{12}O_2$ is at any time, t ,

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3 M_3^0 (1 - e^{-(k_3+k_4)t})}{(k_3+k_4) \left[M_1^0 (1 - e^{-k_1 t}) + M_2^0 (1 - e^{-k_2 t}) \right] + \frac{k_4}{k_3+k_4} M_3^0 (1 - e^{-(k_3+k_4)t})}$$

where M_1^0 , M_2^0 , and M_3^0 are the initial amounts of the malonic acids in Eqs. (1)–(3). If α is the average fraction of C^{13} in natural carbon and if we assume that there is no fractionation in the formation of malonic acid, then we get

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2\alpha k_3}{(1-\alpha)k_1} \text{ at small } t$$

and

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2\alpha k_3}{(1-\alpha)(k_3+k_4)} \text{ at } t = \infty.$$

Implicit in these equations are the approximations that $k_2 \alpha \approx k_1 \alpha$, $k_4 \alpha \approx k_3 \alpha \approx (k_1/2)\alpha$. These assumptions are justified by our results.

C. P. malonic acid was further purified by fractional crystallization from water at about 20°C. The sample used in experiment 2 (M.P. 137–137.5°C) was 99.2 percent pure by acidimetric titration. Samples of the order of 5 grams were decomposed in a thermostated (137.5±0.5°C) vacuum system. The CO_2 was separated from the acetic acid by cold traps. A sample of the CO_2 was collected after a small amount of decomposition and another sample was taken for analysis after completion of the reaction. A portion of the purified malonic acid was oxidized completely to CO_2 by KIO_3 and $K_2Cr_2O_7$ in a mixture of syrupy H_3PO_4 and 30 percent fuming H_2SO_4 . Determination of the ratio of $C^{13}O_2/C^{12}O_2$ from the oxidation gives directly $\alpha/(1-\alpha)$. The samples were analyzed with a Consolidated-Nier isotope ratio mass spectrometer. During the course of analysis frequent determinations were made on samples of tank CO_2 to check the precision and reproducibility of the mass spectrometer. The results are given in Table I. The values of $k_1/2k_3$ were corrected back to zero time. For the calculation of k_4/k_3 the values of $t = \infty$ were corrected for the amount of sample of different isotopic composition removed at t . Our results for tank CO_2 and the CO_2 from the combustion of the malonic acid are in good agreement with each other and the results of Nier and Gulbransen⁴ (0.0111±0.0002). The close agreement between tank CO_2 and the combustion sample justify our assumption in regard to fractionation in the formation of the two C^{13} malonic acids. It should be pointed out that malonic acid sample 1 was purified in a different manner and contained some NaCl, which does not take part in the reaction. The discrepancy between the tank CO_2 analyses as well as the other samples in the two different sets of experiments resulted from the differences

TABLE I.

Exp.	Sample	$C^{13}O_2/C^{12}O_2$	Av. dev.	$k_1/2k_3$	k_4/k_3
1	$t = \epsilon$	0.010587	0.024%	1.039±0.001	
1	Tank CO_2	0.010986	0.024%		
1	$t = \infty$	0.010902	Single Det.		1.020
2	$t = \epsilon$	0.010918	0.008%	1.035±0.001	
2	Tank CO_2	0.011287	0.078%		
2	Combustion	0.011303	0.047%		
2	$t = \infty$	0.011200	0.10%		1.019±0.001
Theory				1.021	1.0198

in the operating characteristics of the spectrometer over a period of several weeks. In any given experiment the reproducibility was excellent as shown by the average deviations, which were usually taken from three or more independent determinations.

The theoretical values were calculated according to the method previously given¹ for C^{14} . The theoretical value for k_4/k_3 is in excellent agreement with experiment. The discrepancy between the theoretical and experimental values for $k_1/2k_3$ results from the fact that the malonic acid vibrations cannot be completely approximated by an XY_2 model. The vibrations within the carboxyl group should be taken into account as both our experiments and those on oxalic acid show. The C^{14} experiments on malonic acid² measure k_4/k_3 in the above notation. Both theory and the C^{13} experiments on oxalic and malonic acids are not consistent with the large isotope effects reported² for C^{14} substitution in malonic and brom-malonic acids.

* Research carried out under the auspices of the AEC.

¹ J. Bigeleisen, J. Chem. Phys. 17, 425 (1949).

² P. E. Yankwich and M. Calvin, J. Chem. Phys. 17, 109 (1949).

³ Lindsay, McElcheran, and Thode, J. Chem. Phys. 17, 589 (1949).

⁴ A. O. Nier and E. A. Gulbransen, J. Am. Chem. Soc. 61, 697 (1939).

Contribution to the Thermodynamics of High Polymer Solutions. V. Solubility of Heterogenous Polymers

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August 19, 1949

IN an article in course of publication¹ we give some results on precipitation limits of narrow fractions and mixtures of fractions of GRS, precipitated by ethanol from toluene solutions. We came to the conclusion that the precipitation limit for mixtures was not determined by the number average molecular weight as previously suggested on the basis of a statistical treatment,² but was dependent on an average of a rather higher order than the weight average.

Lately Stockmayer³ has corrected the results of Scott and has shown that the precipitation limit is determined by the relation

$$2\mu_c = (1 + x_w^{-1/2})^2 - \frac{(x_z^{1/2} - x_w^{1/2})^2}{x_w \cdot x_z^{1/2}}, \quad (1)$$

where x_w is the weight average and x_z the z average of the number of segments.⁴

In the absence of published data Stockmayer could not check his formula experimentally. It was interesting to attempt a verification with our data. To make a rigorous test one would have to determine μ -values independently, say from osmotic pressure measurements, and to make all the comparisons at critical concentrations. This is prohibitively long and the precise determination of the precipitation limit at the rather high critical concentrations is difficult. We have hence proceeded in a different way. A calibration curve, molecular weight, *viz.*, concentration of alcohol at the precipitation point, was established from experiments on narrow fractions, for which $\bar{M}_n \approx \bar{M}_w \approx \bar{M}_z$; the real concentration of the polymer at the precipitation point being $\varphi_P = 1.10^{-2}$. From this plot and the experimentally determined amount of alcohol required for precipitation of mixtures of frac-