

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

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Citation: *The Journal of Chemical Physics* **17**, 999 (1949); doi: 10.1063/1.1747103

View online: <http://dx.doi.org/10.1063/1.1747103>

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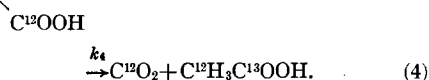
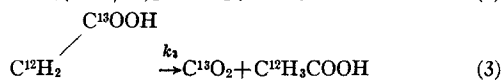
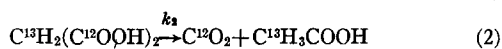
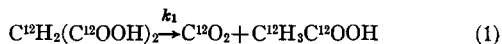
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J. Chem. Phys. **10**, 51 (1942); 10.1063/1.1723621



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	<i>t</i> = ε	0.010587	0.024%	1.039 ± 0.001	1.020
1	Tank CO ₂	0.010986	0.024%		
1	<i>t</i> = ∞	0.010902	Single Det.		
2	<i>t</i> = ε	0.010918	0.008%	1.035 ± 0.001	
2	Tank CO ₂	0.011287	0.078%		
2	Combustion	0.011303	0.047%		
2	<i>t</i> = ∞	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.

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

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Contribution to the Thermodynamics of High Polymer Solutions. V. Solubility of Heterogeneous 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-

No.	Molecular weight of fractions	Composition of the mixture by weight	10^{-3}				
			E.E.M.W.	M_{St}	M_n	M_w	M_z
8	75 20	9.62 90.38	30.0 \pm 1	27.8	21.5	25.3	35.7
9	220 1	88.4 11.6	250 \pm 35	207	8.3	194	220
10	220 1	46.0 54.0	170 \pm 15	148	1.8	101	219
11	220 1	13.15 86.85	125 \pm 10	102	1.15	29.9	189.5