acid at *p*H 3.5,[5,6] Am is found to elute almost in coincidence with Pm, while Cm appears between Sm and Pm. Cf, however, elutes between Dy and Tb with citric acid, but with lactic acid it falls between Tb and Gd.

TABLE I

C RATIOS OBTAINED FOR LANTHANIDE AND ACTINIDE ELEMENTS RELATIVE TO Eu USING LACTIC ACID AT *p*H 3.0 AND 87°

Element	C ratio to Eu	Element	C ratio to Eu
Ho	0.28 ± 0.03[a]	Bk	0.87[b]
Dy	.40 ± .03	Eu	1.000
99	.40 ± .03	Sm	1.28 ± 0.03
Tb	.52 ± .03	Cm	1.58 ± .03
Cf	.63 ± .03	Am	2.00 ± .03
Gd	.845 ± .005	Pm	2.06 ± .03

[a] Standard deviation. [b] Calculated from equation 3.

The superiority of lactic acid to citric acid for separating the trivalent actinide elements is demonstrated by the C ratios (or separation factors) shown in Table II. These data indicate that lactic acid offers a 4% increase in separation per column stage.

TABLE II

A COMPARISON OF SEPARATION FACTORS OBTAINED WITH LACTIC AND CITRIC ACID ELUANTS AT 87° FOR Am, Cm AND Cf

	Citric acid	Lactic acid
$C_{\text{Am}}/C_{\text{Cm}}$	1.21[a]	1.27
$C_{\text{Cm}}/C_{\text{Cf}}$	2.42[a]	2.51

[a] Calculated from the results of Street, Thompson and Seaborg.[6]

According to the data of Thompson, Seaborg and co-workers,[5,6] the relative elution positions of lanthanide and actinide homologs may be related almost as well by a logarithmic as by a linear equation. Thus, if C_{Ac} is the C value of any trivalent actinide element and C_{La} is the C value of its lanthanide homolog, the linear relationship

$$C_{\text{Ac}}/C_{\text{Eu}} = 2.13(C_{\text{La}}/C_{\text{Eu}}) - 0.507 \qquad (1)$$

gives a goodness of fit[7] of 0.008, while the logarithmic equation

$$C_{\text{Ac}}/C_{\text{Eu}} = 1.64(C_{\text{La}}/C_{\text{Eu}})^{1.53} \qquad (2)$$

gives a goodness of fit of 0.010.

With lactic acid, however, the logarithmic equation

$$C_{\text{Ac}}/C_{\text{Eu}} = 1.99(C_{\text{La}}/C_{\text{Eu}})^{1.26} \qquad (3)$$

with a fit of 0.009 is considerably better than the linear equation

$$C_{\text{Ac}}/C_{\text{Eu}} = 2.20(C_{\text{La}}/C_{\text{Eu}}) - 0.236 \qquad (4)$$

with a fit of 0.029.

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[5] S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *ibid.*, **72**, 2798 (1950).

[6] K. Street, Jr., S. G. Thompson and G. T. Seaborg, *ibid.*, **72**, 4832 (1950).

[7] R. Livingston, "Physico Chemical Experiments," The Macmillan Co., New York, N. Y., p. 35.

The Purification and Some Physical Properties of Nitromethane

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In order to make available high-purity nitromethane for thermodynamic measurements, a commercially prepared sample was purified by chemical and physical means to better than 99.9 mole per cent. as determined by the freezing point method. In addition to the thermodynamic properties reported by McCullough, *et al.*,[2] values for freezing point, density, refractive index, viscosity and surface tension were determined on the purified nitromethane. This paper describes the purification procedures and presents values for the latter properties.

Purification.—The nitromethane was a commercially purified sample obtained from Commercial Solvents Corporation. Most of the impurities had been removed, but further necessary purification was effected by a combination of chemical and physical means. The method employed, with only minor deviations, was suggested by John A. Reddick of Commercial Solvents Corporation,[3] and resulted in a sample of better than 99.9 mole per cent. purity as determined by the freezing point method of Rossini.[4]

The nitromethane was given three successive washings with each of the following reagents in order: 25 g. each of sodium bicarbonate and sodium bisulfite per liter of water; 5% sulfuric acid solution and water. Each treatment was accomplished by violent agitation in a separatory funnel. A 2.5-liter sample of the washed nitromethane and 850 ml. of water were charged to an Oldershaw perforated-plate column with a rectifying section 137 cm. in length. After refluxing for 1 hour, 10 ml. of distillate was removed at total takeoff. Refluxing and distillate removal were repeated at 30-minute intervals until the head temperature remained constant, when an additional 10 ml. was collected. All distillate obtained to this point was discarded. The distillation was then continued at a reflux ratio of 5:2 until an increase in head temperature of 1° was observed. The nitromethane then was separated from the azeotropic distillate, which was an immiscible nitromethane–water mixture. This nitromethane was charged to a vacuum-jacketed Podbielniak "Heli-Grid" packed column with a rectifying section 22 mm. by 122 cm. All of the water remaining in the sample was removed by alternate refluxing at 100 mm. pressure and product removal at total takeoff until the boiling point of nitromethane (101.2°) was reached. The coolant to the head condenser was then shut off, and the nitromethane vapors were allowed to flush out the remaining traces of water in both the head and takeoff tube. Refluxing was continued for two hours, 25 ml. of distillate was collected and discarded, and the remainder of the charge was distilled at a reflux ratio of 90:1.

The glassware and column packing were acid washed, and the material was handled in an inert atmosphere and in the absence of strong light. The purified nitromethane was stored under vacuum in glass ampoules containing boric acid and given a vapor-phase transfer immediately before property measurements were made.

Physical Properties

Refractive Index.—Refractive indices (Table I) were measured with a Bausch & Lomb Precision oil refractometer, Abbe type, by procedures previously described.[5] Data

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[1] (a) Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla.; (b) Petroleum and Oil Shale Experiment Station, Laramie, Wyo.

[2] J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, paper presented at Kansas City ACS Meeting, March 23–April 1, 1954.

[3] Private communication.

[4] F. D. Rossini, *Anal. Chem.*, **20**, 110 (1948).

[5] W. E. Haines, R. V. Helm, C. W. Bailey and J. S. Ball, *J. Phys. Chem.*, **58**, 270 (1954).

Table I

Index of Refraction of Nitromethane

Temp., °C.	Wave length, Å.						
	6678.1 (He_r)	6562.8 (H_C)	5892.6 (Na_D)	5460.7 (Hg_e)	5015.7 (He_v)	4861.3 (H_F)	4358.3 (Hg_g)
20	1.37900	1.37944	1.38197	1.38416	1.38705	1.38828	1.39354
25	1.37669	1.37713	1.37963	1.38179	1.38468	1.38588	1.39115
30	1.37442	1.37479	1.37730	1.37948	1.38232	1.38345	1.38874

were obtained at 20, 25 and 30° for seven different wave lengths of light. The temperatures were maintained by circulating water controlled to a maximum variation of ±0.005°. The ambient temperature was maintained to ±1° of the temperature of measurement to minimize heat loss or gain by the prisms. Accuracy of reported values is estimated to be ±0.00006.

Density.—Densities (Table II) were determined at 20, 25 and 30° with a Christian Becker chainomatic five-place specific gravity balance with a five-gram displacement plummet.[5] The accuracy of the measurements is estimated to be ±0.00005 g. ml.$^{-1}$. The equation $d_t = 1.16448 - 0.001351t$ expresses the density–temperature relationship over the range of 20 to 30°.

Table II

Properties of Nitromethane

Temp., °C.	Density, g./ml.	Abs. vis., cp.	Surface tension, dynes/cm.
20	1.13749	0.646	37.5
25	1.13064	.608	36.7
30	1.12398	.574	35.9

Viscosity.—Viscosities (Table II) were determined at 20, 25 and 30° using two Geist–Cannon viscometers designed for non-viscous fluids.[6] At least two consecutive efflux times agreeing to within 0.1 second were obtained on both viscometers controlled in a bath to ±0.005°.[5] The reported values are referred to a value of 1.002 centipoises for water at 20°,[7] the precision of the measurements is ±0.03% and the accuracy is estimated to be ±0.001 centipoise.

Surface Tension.—Surface tensions were measured at 20, 25 and 30° in capillarimeters of U-tube design as previously described.[5] Capillary rise was measured by means of a cathetometer on the sample controlled to ±0.005°. These values are referred to a value of 28.88 dynes cm.$^{-1}$ for benzene at 20°.[8] Accuracy of the reported values is estimated to be ±0.2 dyne cm.$^{-1}$.

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[6] J. M. Geist and M. R. Cannon, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 611 (1946).

[7] J. F. Swindells, J. R. Coe, Jr., and T. B. Godfrey, *J. Research Natl. Bur. Standards*, **48**, 1 (1952).

[8] "International Critical Tables," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1928, p. 54.

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The Kinetics of the Knoevenagel–Doebner Reaction

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The reaction of benzaldehyde with malonic acid in the presence of piperidine was studied in pyridine and in pyridine–cyclohexanone solutions. The condensation was shown to follow over-all second-order reaction kinetics. The decarboxylation curves of the condensation product in the original reaction mixture, after an induction period, seem to conform to a first-order kinetic equation, as does the decarboxylation of benzalmalonic acid itself in pyridine. It is shown that the general methods used for the description of the kinetics of consecutive reactions cannot be applied for the case considered. The role of the catalyst and that of the two solvents used is discussed.

The Knoevenagel–Doebner modification of the Perkin cinnamic acid synthesis[2] has been the subject of only very few quantitative kinetic studies,[3] although a number of papers deal with the mechanism of the reaction.[4–12] The previous investigations made no attempt to determine the exact rate of both the carbonyl–methylene condensation and the subsequent decarboxylation. In the present paper we followed the kinetics of the condensation by means of the Karl Fischer water-determination method,[13] and measured volumetrically the evolution of carbon dioxide from the reaction mixture. Analysis of the kinetic results has shown that the two reactions cannot be adequately described by the methods applicable for simple irreversible consecutive reactions[14,15] and, accordingly, the reaction must be a more complex one than generally accepted.

Experimental

Materials Used.—Pure commercial malonic acid (Eastman Kodak Co., white label, m.p. 134–135°) was used without purification. After drying to constant weight in a desiccator, it contained about 0.15% water. The benzaldehyde was twice distilled fractionally before use. It contained 0.2% water. The pyridine (B.D.H., redistilled)

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[2] For a review of the literature up to 1940, see J. R. Johnson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 210–265.

[3] (a) E. F. Pratt and E. Werble, This Journal, **72**, 4638 (1950); (b) E. J. Corey, *ibid.*, **74**, 5897 (1952).

[4] E. Knoevenagel, *Ber.*, **31**, 2596 (1898).

[5] W. M. Rodionov, This Journal, **51**, 847 (1929).

[6] A. C. Cope, *ibid.*, **59**, 2327 (1937).

[7] R. Kuhn, W. Badstuebner and C. Grundmann, *Ber.*, **69B**, 98 (1936).

[8] S. Dutt, *Quart. J. Chem. Soc.*, **1**, 297 (1925).

[9] M. Dalal and S. Dutt, *J. Indian Chem. Soc.*, **9**, 309 (1932).

[10] K. C. Blanchard, D. L. Klein and J. MacDonald, This Journal, **53**, 2809 (1931).

[11] C. A. VanderWerf, *Trans. Kansas Acad. Sci.*, **50**, 356 (1947).

[12] T. S. Wheeler, *Irish Chem. Assoc. J.*, **5** (1947–1948).

[13] J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

[14] J. Chien, This Journal, **70**, 2256 (1948).

[15] S. W. Benson, *J. Chem. Phys.*, **20**, 1605 (1952).