extent of conversion involved in a given number of rate measurements by a factor of more than 100.

This combined method has been used in evaluating the ratio of the velocity coefficients of propagation to termination (k_p/k_t) at 25° C. for the polymerizations of acrylonitrile in dimethyl formamide solution (30/70 : : v/v) initiated with $3{\cdot}8 \times 10^{-3}$ moles/l. azo-*bis-iso*butyronitrile, and of vinyl chloride initiated by 8×10^{-2} moles/l. bromotrichloromethane. The values obtained were $3{\cdot}4 \times 10^{-6}$ and $7{\cdot}1 \times 10^{-7}$ respectively. Values of the ratio of the sectored to unsectored rate for a number of different flash times obtained in vinyl chloride polymerization are given together with the theoretical plot in Fig. 1. It will be seen that the experimental points lie mainly on the theoretical curve and that the agreement is better than is often obtained in the normal sector method.

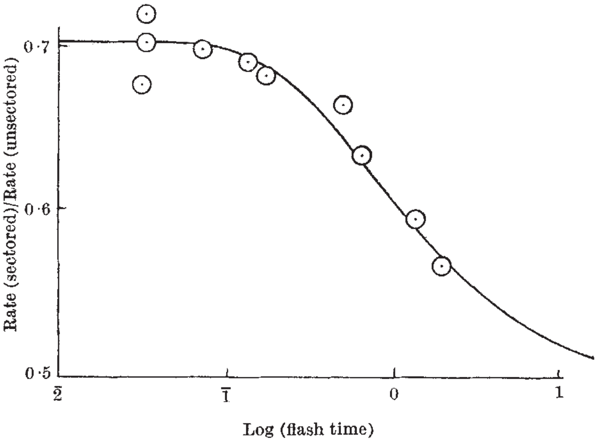

Fig. 1. Ratio of 'sectored' to 'unsectored' rates against log (flash time) for the polymerization of vinyl chloride at 25° C. ⊙, Experimental points ; —, theoretical curve

We express our thanks to Prof. P. D. Ritchie for his interest in the work, to the Department of Scientific and Industrial Research for maintenance awards to two of us (S. A. M. and R. A. M. T.) and to the Distillers Co. for a gift of vinyl chloride.

W. I. BENGOUGH
S. A. MCINTOSH
R. A. M. THOMSON

Department of Chemical Technology,
Royal College of Science and Technology,
Glasgow.

June 3.

---

[1] Burnett and Melville, *Proc. Roy. Soc.*, A, **189**, 456 (1947).
[2] Majury and Melville, *Proc. Roy. Soc.*, A, **205**, 496 (1951).
[3] Grassie and Melville, *Proc. Roy. Soc.*, A, **207**, 285 (1951).
[4] Bengough and Melville, *Proc. Roy. Soc.*, A, **225**, 330 (1954).
[5] Miyana, *Bull. Chem. Soc. Japan*, **29**, 711 (1956).
[6] Bengough, *Trans. Farad. Soc.*, **54**, 868 (1958).

Thermal Decarboxylation of Some Keto-Acid Hydrazones

THE 2,4-dinitrophenylhydrazones of keto-acids are frequently used to identify these metabolic intermediates. The clear statement by Clift and Cook[1] regarding the ready thermal decarboxylation of the 2,4-dinitrophenylhydrazones of oxaloacetic and acetoacetic acids has sometimes been overlooked, particularly in the use of melting points as a means of identification. Some of our observations bear on the problem.

Oxaloacetic acid-2, 4-dinitrophenylhydrazone (I), synthesized by the usual procedure, when inserted into a bath at about 190°C. or above, melted with vigorous bubbling and resolidified immediately, with a final melting point of 214°C. The substance after resolidification (II) was re-analysed by paper chromatography (*n*-butanol/ethanol/0·5 *M* ammonium hydroxide 7:1:2 in the dark) and was recrystallized. After paper chromatography the spot was eluted and examined spectrophotometrically. Authentic samples of *trans* (III) and *cis* (III*a*) pyruvic acid-dinitrophenylhydrazone were prepared by the method of Katsuki *et al.*[2] As shown in Table 1, (I) was decarboxylated to pyruvic acid-dinitrophenylhydrazone (chiefly *trans*) under these conditions. When (I) was heated slowly from a lower temperature, for example, 100°C., double melting was not observed and only the melting point of 214°C. was obtained. Under these conditions, too, chromatography showed that most of the hydrazone was converted to (III) during the longer heating.

Table 1. PROPERTIES OF 2, 4-DINITROPHENYLHYDRAZONES.

Substance	R_F	Melting point (deg. C., corr.)	λmax.(mμ)
I	0·05, 0·11	214 (final)	450
II	0·55*	217	446
III	0·55	217†	446
III*a*	0·66	‡	416, 530
IV	0·57	123 (final)	433, 528
V	0·95	123	430, 528
VI	0·95	123†	430, 528

* With large sample a weak spot of *cis*-pyruvic acid-dinitrophenylhydrazone was also found.
† Mixed melting point of II and III, 217°C.; of V and VI, 123°C.
‡ Melting point not sharp because of thermal isomerization to *trans* form.

When acetoacetic acid-2, 4-dinitrophenylhydrazone (IV) was placed in the bath at about 115°C. or above, it melted, bubbled, and resolidified; the final melting point was 123°C. The resolidified material after recrystallization (V) also melted at 123°C. Thus, (V) is acetone-2, 4-dinitrophenylhydrazone as shown by comparison with an authentic sample (VI). This conversion also took place when the heating was done slowly from a lower temperature, but only a single melting at 123°C. was observed.

The melting point of the 2, 4-dinitrophenylhydrazones is not a reliable criterion for confirmation or identification of oxaloacetic or acetoacetic acids. Resolidification during melting-point determination was observed by Snell[3] with α-ketoisocaproic acid—dinitrophenylhydrazone but no explanation was suggested.

This investigation was supported by Grant *C*-4342 from the National Cancer Institute, U.S. Public Health Service.

AMBROSE M. TOKUSHIGE
ELTON S. COOK

Division of Chemistry and Biochemistry,
Institutum Divi Thomae,
Cincinnati, Ohio.

May 26.

---

[1] Clift, F. P., and Cook, R. P., *Biochem. J.*, **26**, 1800 (1932).
[2] Moriwaki, T., Katsuki, H., and Tanaka, S., *J. Chem. Soc. Japan*, **76**, 1367 (1955).
[3] Metzler, D. E., Olivard, J., and Snell, E. E., *J. Amer. Chem. Soc.*, **76**, 644 (1954).