water; Monsanto Chemicals (Australia), Ltd., for financial support; J. Mason for instrumentation advice, and Mr. L. James for optical rotation measurements.

G. E. CALF
J. L. GARNETT
Department of Physical Chemistry,
University of New South Wales, Sydney.
B. H. HALPERN
K. TURNBULL
The John Curtin School of Medical Research,
Australian National University, Canberra.

[1] Garnett, J. L., *Nucleonics*, **20**, 86 (1962).
[2] Wilzbach, K. E., *J. Amer. Chem. Soc.*, **79**, 1013 (1957).
[3] Crawford, B. R., and Garnett, J. L., in *Proc. Intern. Atomic Energy Tritium Symp.*, *Vienna*, **2**, 10 (1961).
[4] Angyal, S. J., Garnett, J. L., and Hoskinson, R. M., *Nature*, **197**, 485 (1963).
[5] Angyal, S. J., Garnett, J. L., and Hoskinson, R. M., *Austral. J. Chem.*, **16**, 252 (1963).
[6] Garnett, J. L., Halpern, B., Law, S. W., and Turnbull, K. (to be published).
[7] Bell, J., Macdonald, K. A., and Reed, R. I., *J. Chem. Soc.*, 3456 (1953).
[8] Garnett, J. L., and Sollich, W. A., *J. Catalysis*, **2**, 350 (1963).
[9] Garnett, J. L., and Sollich, W. A., *Nature*, **201**, 902 (1964).
[10] Garnett, J. L., and Sollich, W. A., *Austral. J. Chem.*, **18**, 1003 (1965).
[11] Garnett, J. L., and Sollich-Baumgartner, W. A., *J. Phys. Chem.*, **68**, 1850 (1965).
[12] Garnett, J. L., and Sollich-Baumgartner, W. A., *J. Phys. Chem.*, **68**, 3177 (1964).
[13] Brown, W. G., Garnett, J. L., and Van Hook, O. W., *J. Phys. Chem.*, **68**, 3064 (1964).
[14] Crawford, B. R., and Garnett, J. L., *Austral. J. Chem.*, **18**, 1951 (1965).

Stereospecific Addition of Hydrogen to Fumaric Acid in Irradiated Single Crystals of Succinic Acid

Pooley and Whiffen[1] reported an interesting proton–deuteron exchange reaction of the primary radical $HOOCCH_\beta H_{\beta'}CH_\alpha COOH$ (or $DOOCCH_\beta H_{\beta'}CH_\alpha COOD$)[2] in an irradiated crystal of succinic acid. By means of an electron spin resonance technique, they detected $DOOCCD_\beta H_{\beta'}CHCOOD$ in addition to the primary species, but they did not detect $DOOCCH_\beta D_{\beta'}CHCOOD$, nor $DOOCCH_2CDCOOD$ (hyperfine splitting constant for H_β is larger than that for $H_{\beta'}$[2]). It was shown later[3,4], however, that formation of this $DOOCCD_\beta H_{\beta'}CHCOOD$ species is associated with an unidentified impurity in the crystal; the impurity is too low in concentration to be detected with ordinary experimental techniques. During the present investigation it was found that fumaric acid behaved quite similarly to the impurity: in a crystal of succinic acid which contained 0·001 mole fraction of fumaric acid, the ratio

$$[DOOCD_\beta H_{\beta'}CHCOOD]/[DOOCCH_2CHCOOD]$$

was found to be 0·2, that is, the same as the ratio found in the impure crystal[3].

The crystals used in this investigation were grown by slowly cooling aqueous solutions of mixtures of succinic acid and fumaric acid. Heavy water was used for the deuterium-substituted crystals. Concentrations of fumaric acid in the crystals were estimated from those of their mother liquors. The relation between the concentration of fumaric acid in the crystal and that in its mother liquor was determined by means of radioactive fumaric acid $HOOCC^*H = C^*HCOOH$. Irradiation of the crystals was accomplished by an X-ray source (30 kV, 15 m.amp) at room temperature, and the concentration of the radicals was about 7×10^{-4} radical/molecule. The electron spin resonance absorption was measured at 9 Gc/s at room temperature.

In any crystals which were grown from the aqueous solutions, only the primary species was detected. In the deuterium substituted crystal, which contained more than a 0·0001 mole fraction of fumaric acid, the $DOOCCD_\beta H_{\beta'}CHCOOD$ species was detected, in addition to the primary species. When 2,3-deuterofumaric acid was used, the absorption from $DOOCCD_2CDCOOD$ replaced this absorption. Thus, it was concluded that the radical

$DOOCCD_\beta H_{\beta'}CHCOOD$ was formed by addition of hydrogen (deuterium) to fumaric acid.

Concentration of $DOOCCD_\beta H_{\beta'}CHCOOD$ increased with increasing concentration of fumaric acid in the crystal, until the latter concentration became about 0·01 mole fraction. For the crystal in which the concentration of fumaric acid was higher than 0·01, ratio

$$[DOOCCD_\beta H_{\beta'}CHCOOD]/[DOOCCH_2CHCOOD]$$

was found to be about 0·65.

From the signal-to-noise ratio of the absorption pattern of the crystal, the ratio

$$[DOOCCH_\beta D_{\beta'}CHCOOD]/[DOOCCD_\beta H_{\beta'}CHCOOD]$$

was found to be less than 1/300. In an isolated molecule of fumaric acid, these two species should have been formed with an equal reaction rate. Therefore, there was no uncertainty that this large difference in the addition rates arose from the crystal field which surrounded the molecule of fumaric acid. Such an effect of the crystal field on a chemical reaction had already been reported in the case of proton–deuteron exchange reaction of the radical in irradiated crystals of D,L-aspartic acid[4,5].

So far as we know, a high stereospecific efficiency, such as that observed at present, has been found only in the case of enzymatic reactions[6]. Moreover, it is well known that an enzyme is highly selective in its reactions. Such high selectivity was also found in the present case. So far as our examination was concerned, fumaric acid was the only compound from which a radical was formed with the use of an irradiated crystal of succinic acid. The other compounds examined (inactive compounds), which are more or less similar to fumaric acid in structure, were as follows: maleic acid, oxalic acid, crotonic acid, acrylic acid, tartaric acid, and D,L-aspartic acid. It was not known, however, whether a crystal, grown from a solution containing one of the inactive compounds in addition to succinic acid, contained a significant concentration of molecules of this compound.

We thank Prof. W. Gordy for his advice, and Prof. N. Tamiya for supplying 2,3-deuterofumaric acid.

ICHIRO MIYAGAWA *
Department of Physics,
Duke University,
Durham, North Carolina.
KOICHI ITOH
Institute for Solid State Physics,
University of Tokyo, Japan.
* Present address: Department of Physics, University of Alabama, Alabama.

[1] Pooley, D., and Whiffen, D. H., *J. Chem. Soc.*, 366 (1962).
[2] Heller, C., and McConnell, H. M., *J. Chem. Phys.*, **32**, 1535 (1960). Pooley, D., and Whiffen, D. H., *Mol. Phys.*, **4**, 81 (1961).
[3] Miyagawa, I., and Itoh, K., *Bull. Amer. Phys. Soc.*, Ser. II, **9**, 488 (1964).
[4] Itoh, K., thesis, Univ. Tokyo (1965).
[5] Miyagawa, I., and Itoh, K., *J. Chem. Phys.*, **43**, 2915 (1965).
[6] For a review see, for example, Gutfreund, H., in *The Enzymes*, edit. by Boyer, P. D., Lardy, H., and Myrbäck, K., **1**, 233 (Academic Press, Inc., 1959).

Anomalies in Contact Angle Behaviour for Ethyl Alcohol–Water Mixtures

MEASUREMENTS of static contact angles for alcohol/water mixtures on pretreated copper surfaces are presented in Fig. 1. The results indicate that, for ethyl alcohol concentrations up to 8 per cent by weight, a constant contact angle of 72° is attained. Analogous behaviour has been observed by Franke[1] when measuring mutual diffusivities where a minimum value was reported at 10 per cent concentration. Hoffman *et al.*[2] have shown a maximum value of the temperature coefficient of the surface tension of ethyl alcohol/water mixtures at 8 per cent weight.