

## The Transition State in Gas-phase Elimination from Halides

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INGOLD and his co-workers<sup>1</sup> unmistakably demonstrated the role of dissociated carbonium ions in reactions proceeding by the unimolecular mechanism in polar solvents ( $S_N1$  and  $E1$ ). In later work Winstein and his school<sup>2</sup> elaborated this scheme by introducing the concept of ion-pair return from two discrete varieties of ion pairs:<sup>3</sup> the contact (or intimate) ion pair  $R^+X^-$  and the solvent-separated ion pair  $R^+ \parallel X^-$ . The necessity for this additional hypothesis arose from the fact that for many systems, the polarimetric rate constant of a substrate ( $k_\alpha$ ) was appreciably greater than the rate of substitution ( $k_i$ ). In view of the postulated

analogy between gas-phase elimination from halides ( $E_g$ ) and the  $S_N1$  or  $E1$  reactions of the corresponding halides,<sup>4</sup> it was thought of interest to probe for a possible intervention of contact ion-pairs in gas-phase eliminations. We report rate measurements for elimination of hydrogen chloride from 2-chloro-octane and also the rate of loss of optical activity by D-(+)-2-chloro-octane. The elimination was essentially homogeneous, followed a first-order law, and no inhibition of the reaction was observed when runs were done in the presence of propene or cyclohexene. The rate constants in the temperature range 325—385° were fitted to

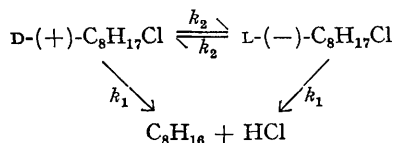
TABLE 1

*A comparison of mean values of  $k_1$  and  $(k_1 + 2k_2)$*

| $T$    | No. of runs | $10^4(k_1 + 2k_2)$ (sec. <sup>-1</sup> ) | No. of runs | $10^4k_1$ (sec. <sup>-1</sup> ) |
|--------|-------------|--|-------------|---------------------------------|
| 358.2° | 5           | 4.60                                     | 40          | 4.49                            |
| 338.5° | 5           | 1.39                                     | 11          | 1.32                            |
| 326.5° | 3           | 0.61                                     | 8           | 0.60                            |

the equation  $\log k_1 = 13.53 - 48,700/2.303RT$ . By analogy with halides previously studied, the reaction may be taken to be unimolecular.

For the reaction scheme



it can be shown that  $\alpha_t/\alpha_0 = \exp -(k_1 + 2k_2)t$ , when  $\alpha_t$  and  $\alpha_0$  are the rotations at time  $t$  and zero respectively. This enables  $(k_1 + 2k_2)$  to be calculated from  $\alpha_t/\alpha_0$  and  $t$ . The values of  $(k_1 + 2k_2)$  obtained at three temperatures are shown in Table 1, together with values of  $k_1$  derived from  $k_1 = (1/t)\ln p_0/(2p_0 - P_t)$  where  $p_0$  is the initial pressure of chloride and  $P_t$  is the total pressure at time  $t$ . In view of the experimental errors involved, the conclusion to be drawn from the Table is that  $k_1 \gg k_2$ . This point is further borne out by an examination of the optical purity of the substrate during the course of the reaction, namely the ratio  $\alpha_t/\alpha_0(1-f)$  where  $f$  is the fraction of substrate consumed at time  $t$ . Results at 338.5°

are shown in Table 2. The average value of  $\alpha_t/\alpha_0(1-f)$  from fifteen experiments was 0.991 (theoretical value for no racemisation is unity assuming that  $k_1 \gg k_2$ ).

TABLE 2

*The specific rotation of 2-chloro-octane as a function of time*

| Time (sec.) | (1-f) | $\alpha_t/\alpha_0$ | $\alpha_t/\alpha_0(1-f)$ |
|-------------|-------|---------------------|--------------------------|
| 1800        | 0.788 | 0.760               | 0.97                     |
| 3600        | 0.622 | 0.605               | 0.97                     |
| 5400        | 0.491 | 0.480               | 0.97                     |
| 7200        | 0.387 | 0.395               | 1.02                     |

While it seems clear that the present situation need not apply for substrates producing more stabilised carbonium ions, our results are consistent with previous evidence<sup>5</sup> for a transition state which is moderately ionic and involving C-X bond extension with polarisation. For racemisation to occur, further separation would be necessary without the virtual halide ion selecting the hydrogen with which it is going to eliminate, and this is apparently energetically unfavourable.

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<sup>1</sup> For a general review of the development of these ideas, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Bell, London, 1953.

<sup>2</sup> See for example, S. Winstein, B. Appel, R. Baker, and A. Diaz, "Organic Reaction Mechanisms", *Chem. Soc. Special Publ.*, 1965, No. 19.

<sup>3</sup> For recent physical observations of these two species, see T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 318.

<sup>4</sup> A. Maccoll and P. J. Thomas, *Nature*, 1955, **170**, 392.

<sup>5</sup> H. M. R. Hoffmann and A. Maccoll, *J. Amer. Chem. Soc.*, 1965, **87**, 3774.