Catalytic Action of a Polybase on an Elimination Reaction of Chloromaleate and Chlorofumarate

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Summary The bimolecular elimination reaction of chloromaleate and chlorofumarate has been studied in the presence of a polybase, poly(dimethyldiallylammonium chloride).

LARGE primary salt effects in inorganic reactions between like-charged ionic species have recently been reported for synthetic and biologically important polyelectrolytes.[1-3] We report here the salt effect of a polybase, poly(dimethyldiallylammonium chloride) (DMC),[4] in another reaction between charged ionic species. The reactions studied were the bimolecular eliminations of chloromaleate and chlorofumarate with hydroxide ion.[5,6] Tetramethylammonium hydroxide (TMAOH) was used as alkali.

It is seen from the Figure that DMC accelerates the reaction considerably, in contrast with tetramethylammonium chloride (TMACl) which showed a negligibly small primary salt effect. Furthermore, the acceleration factor (k_2/k_{20}) of the maleate was larger than that of the fumarate under the same conditions (compare M-2′ with F-2, or M-2 with F-2′).

The primary salt effects are accounted for by Brønsted's theory:[7]

$$k_2/k_{20} = f_A \cdot f_B / f_X$$

where f is the activity coefficient, A and B are the reactants, and X is the intermediate complex. Since it is highly probable that the f values of maleate and fumerate are virtually equal, the present experimental finding $[(k/k_0)_{maleate} > (k/k_0)_{fumarate}]$ indicates that the intermediate produced from the *cis*-isomer has a different stability from that of the *trans*-isomer.

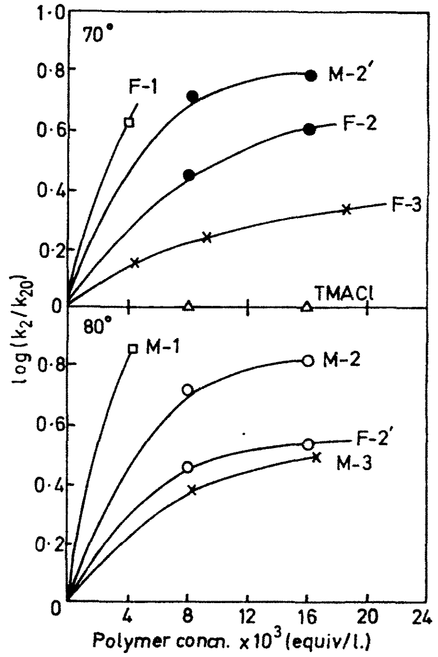

FIGURE. *Primary salt effects on* E_2 *reaction of chlorofumarate and chloromaleate. F and M stand for the fumarate and maleate respectively. Initial concentrations of reactants*: *curve* 1, 2×10^{-3} M; *curve* 2 *and* 2′, 4×10^{-3} M; *curve* 3, 8×10^{-3} M. *The* k_{20} *values of the fumarate at* 70° *were* $3{\cdot}7 \times 10^{-2}$, $3{\cdot}2 \times 10^{-2}$, *and* $3{\cdot}2 \times 10^{-2}$ M^{-1} min^{-1} *at initial concentrations of reactants of* 8×10^{-3}, 4×10^{-3}, *and* 2×10^{-3} M, *respectively, and those of maleate at* 80° *were* $1{\cdot}8 \times 10^{-2}$, $1{\cdot}5 \times 10^{-2}$, *and* $1{\cdot}5 \times 10^{-2}$ M^{-1} *min*$^{-1}$ *at reactant concentrations of* 8×10^{-3}, 4×10^{-3}, *and* 2×10^{-3} M. *At* 4×10^{-3} M, *the* k_{20} *value of the maleate at* 70° *was* $4{\cdot}7 \times 10^{-3}$ M^{-1} *min*$^{-1}$, *and that of the fumarate at* 80° *was* $9{\cdot}0 \times 10^{-2}$ M^{-1} *min*$^{-1}$.

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