An Elimination Reaction with Kinetics Characteristic of the ElcB Mechanism[1]

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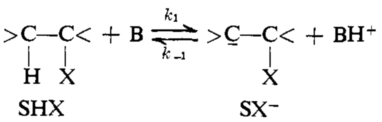
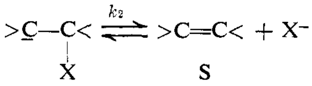
Abstract: The dehydrochlorination of *erythro*-4,4′-dichlorochalcone dichloride, in absolute ethanol at 25°, is subject to general base catalysis. The rate is a nonlinear function of the buffer concentration. The reaction is inhibited by acid. The *trans*-elimination product is predominantly formed from the *erythro* as well as from the more reactive *threo* substrate. A two-step mechanism, involving ionization followed by uncatalyzed cleavage of the carbanion, is consistent with the kinetics. Unless the carbanion is extremely short lived, however, some other explanation of the observed acid inhibition is required, since extensive deuterium exchange in the substrate does not take place.

In 1933, Hughes, Ingold, and Patel[2] stated that the elimination reaction of a tetraalkylammonium ion SHX in basic solution (B = OH^-, X = R_3N) might,



$$\underset{\text{SHX}}{>\underset{\text{H}}{\text{C}}\text{—}\underset{\text{X}}{\text{C}}<} + \text{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{SX}^-}{>\underline{\text{C}}\text{—}\underset{\text{X}}{\text{C}}<} + \text{BH}^+ \tag{1}$$



$$>\underset{\text{X}}{\underline{\text{C}}}\text{—C}< \overset{k_2}{\rightleftharpoons} \underset{\text{S}}{>\text{C}=\text{C}<} + \text{X}^- \tag{2}$$

in certain cases, proceed *via* the carbanion SX^-. This mechanism involving the conjugate base of the substrate was later designated ElcB.[3,4] At that early date, it was recognized that this type of reaction would show a dependence of rate on hydrogen ion concentration different from that expected of a concerted, E2 elimination. In fact, retardation by acid had already been observed in the case of N,N,N-trimethyl-N-(*p*-nitrophenethyl)-ammonium iodide,[5] though the reason for the effect was not unambiguous,[4b] and later studies have failed to support the carbanion mechanism for the Hofmann elimination in strong base.[6]

The most frequently employed criterion of the ElcB mechanism has been deuterium exchange in the unreacted substrate, suggested by Skell and Hauser[7] and observed in a few cases.[8] Its users have been well aware of the fact that appreciable exchange will not take place if the carbanion dissociates to products much faster than it is reprotonated to substrate.[4,7,9] Positive results with this method indicate that the carbanion is present and very probably[10] is an intermediate in the elimination. Negative results, though admittedly usually due to the concerted or E2 mechanism, do not rule out the ElcB nor necessarily prove that it is experimentally indistinguishable from the E2 type; lack of exchange only places a lower limit, depending on the experimental uncertainty, upon the ratio dissociation rate/protonation rate.

Stereochemical factors[4a,c] are most evident when the impossibility of *trans* elimination results in very greatly reduced dehydrohalogenation rates.[11] However, the mechanism of the slow elimination may be carbanion or concerted.[12,13]

Isotope effects[4] and ingenious studies of elimination/substitution product ratios as influenced by structure[14] have been used to estimate the amount of "carbanion character" in concerted but nonsynchronous base-promoted elimination mechanisms, especially with β-phenylethyl bromide and related compounds.

There is much more information to be gleaned from studies of an ElcB reaction than mere second-order kinetics. If the rate constants k_1, k_{-1}, and k_2 are in the proper range, the complex dependence of rate both on pH and on buffer (general acid and base) concentration given by the steady-state equation (eq 3) should be observed. Here k_1^{B} is the second-order rate constant of step 1 when the base is B. The sum in the numerator is

$$k = \frac{k_2 \sum k_1^{\mathrm{B}}[\mathrm{B}]}{k_2 + \sum k_{-1}^{\mathrm{BH}}[\mathrm{BH}^+]} \tag{3}$$

equal to the rate of ionization of the substrate SHX as it reacts with the various bases, B, in the system (eq 1). The two terms in the denominator arise from the two paths available to the carbanion SX^-, dissociation to products (eq 2) or protonation by any of the acids, BH^+, back to SHX. Because the catalytic constants, k_1^{B} and k_{-1}^{BH}, and the dissociation constant of the substrate,

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[1] Preliminary report: T. I. Crowell, A. A. Wall, R. T. Kemp, and R. E. Lutz, *J. Amer. Chem. Soc.*, **85**, 2521 (1963).

[2] E. D. Hughes, C. K. Ingold, and C. S. Patel, *J. Chem. Soc.*, 526 (1933).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 422–423.

[4] For reviews, see (a) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., London, 1963; (b) H. Hine, R. Weisboeck, and O. B. Ramsay, *J. Amer. Chem. Soc.*, **83**, 1222 (1961); (c) J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962); (d) W. H. Saunders, Jr., "The Chemistry of Alkenes" S. Patai, Ed., Interscience Publishers, Inc., London, 1964, Chapter 2.

[5] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 523 (1933).

[6] D. V. Banthorpe and J. H. Ridd, *Proc. Chem. Soc.*, 365 (1964); A. N. Bournes and P. J. Smith, *ibid.*, 366 (1964).

[7] P. S. Skell and C. R. Hauser, *J. Amer. Chem. Soc.*, **67**, 1611 (1945).

[8] L. C. Leitch and H. J. Bernstein, *Can. J. Res.*, **28B**, 35 (1950), and later examples cited in ref 4a.

[9] J. Hine, R. D. Weimar, Jr., P. B. Langford, and O. B. Ramsay, *J. Amer. Chem. Soc.*, **85**, 3894 (1963); G. Marchese, G. Modena, and F. Naso, *Chem. Commun.*, **15**, 492 (1966).

[10] See ref 4b. However, see R. Breslow, *Tetrahedron Lett.*, 399 (1964); also H. M. R. Hoffmann, *ibid.*, **45**, 4393 (1967).

[11] S. J. Cristol, *J. Amer. Chem. Soc.*, **69**, 338 (1947).

[12] S. J. Cristol and F. R. Stermitz, *ibid.*, **82**, 4692 (1960). S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **27**, 293 (1962).

[13] C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Amer. Chem. Soc.*, **84**, 1314 (1962); H. Kwart, T. Takeshita, and J. C. Nyce, *ibid.*, **86**, 2606 (1964); N. A. LeBel, *et al.*, *ibid.*, **85**, 3199 (1963).

[14] (a) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 5 (1964); (b) G. M. Fraser and H. M. R. Hoffmann, *ibid.*, *Sect. B*, 265 (1967).

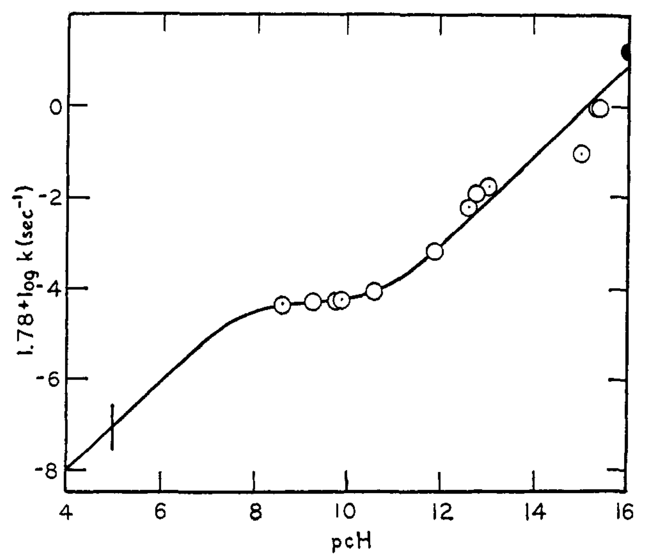
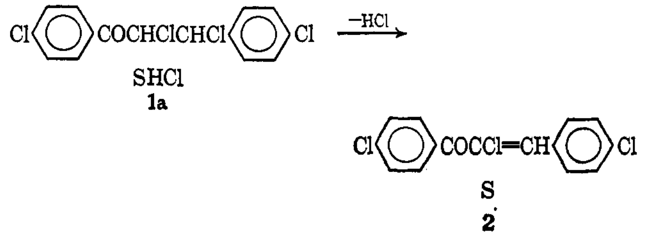


Figure 1. pcH-rate profile (ethanol).

K_{SHX}, are not all independent, eq 4, less obvious than eq 3 but containing fewer constants, is obtained.[15]

$$k = \frac{k_2K_{SHX}\sum k_1^B[B]}{k_2K_{SHX} + [H]^+\sum k_1^B[B]} \qquad (4)$$

In the belief that more detailed kinetic evidence for the ElcB reaction would be desirable,[16] we investigated the elimination of hydrogen chloride from *erythro*-4,4′-dichlorochalcone dichloride (**1a**).



SHCl
1a

S
2

Results

The reaction was studied in absolute ethanol at 25°, over the pcH range 5-17.[17] *trans* product (S) predominated if light was carefully excluded, otherwise about 30% *cis* S was produced. The pseudo-first-order rate constants, *k*, calculated from the total product concentration obtained by ultraviolet spectrophotometry at the isosbestic point of *cis* and *trans*, were unaffected by diffuse light.

The outstanding features of this elimination reaction are that it is very fast in dilute sodium ethoxide, proceeds at a measurable rate in neutral ethanol, and is *inhibited by acid.* The last two facts together suggest the two-step carbanion mechanism; if the base B in neutral or acid solution is assumed to be ethanol, and not ethoxide ion, the concentration of which is less than 3×10^{-10} *M*,[18] then the rate of an E2 reaction would be pH independent, not acid inhibited. A plot of log *k* *vs.* pcH is shown in Figure 1. The vertical line at pcH 5 is a rough estimate of the extremely low rate in 10^{-5} *M* ethanolic HCl. The points in the pcH range 8-12 represent values of *k* extrapolated to zero buffer concentration, from results obtained using sodium acetate–acetic acid buffers. The points near pcH 13 were similarly determined with sodium veronalate–veronal buffers. Unbuffered sodium ethoxide was used for high pcH values. At pcH 15.3, the half-life was less than 1 min. The reaction was nevertheless observed between 40 and 90% completion.

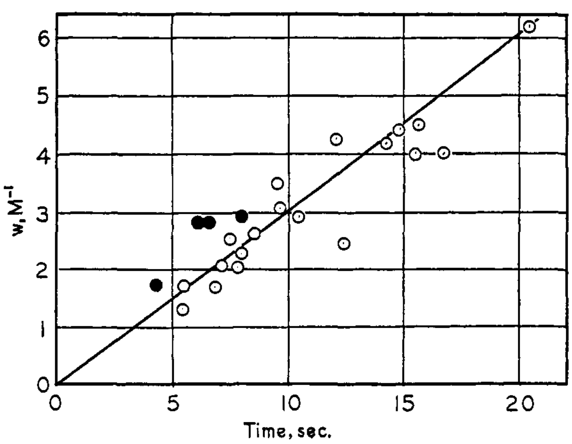


Figure 2. Rate of acid formation by indicator method. Second-order plot, with $w = [10^{-3}/(a - b)] \ln b(a - x)/a(b - x)$. Room temperature (○) and 25° thermostat (●).

Near pcH 16, the rate of consumption of base was observed by means of indicators.[19] A reaction mixture 0.0003-0.0007 *M* in NaOEt and 0.0008-0.004 *M* in SHCl was initially basic to phenolphthalein. After 5-10 sec, the pink color suddenly faded to colorless. Assuming that the ethoxide ion concentration at this time had decreased to 1.6×10^{-4}, corresponding to the pK_a of phenolphthalein,[20] and that the indicator equilibrated rapidly with the system at this pcH, each such observation gave a point on a graph of concentration *vs.* time, calculated as second order in Figure 2. (A first-order plot was more nearly linear, but the reason for this is obscure. The other experiments demonstrate that the rate is proportional to ethoxide ion concentration.) The second-order rate constant from Figure 2 is 3.0×10^2 M^{-1} sec^{-1}, plotted as the dark circle in Figure 1. Single determinations with other indicators[21] gave the following results: thymol blue, pK_a = 15.2, end point corresponding to 84% reaction, $k_1^{OEt} = 6 \times 10^2$ M^{-1} sec^{-1}; phenol red, 13.6, 99.5%, 13×10^2; bromothymol blue, 13.2, 99.8%, 5×10^2. Work with these last two indicators would have to be extended before any significance could be attached to the results.

The highest ethoxide ion concentration used was 0.01 *M* (pcH 17). Two seconds after introducing the substrate SHCl, the reaction was quenched with dilute nitric acid. Spectrophotometric analysis and titration for chloride both indicated that the reaction had gone to completion in this time. Introduction of bromine after reaction with sodium ethoxide yielded the dibromide of the elimination product.[19]

[15] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp 134-135.

[16] R. Breslow, *Tetrahedron Lett.*, 399 (1964).

[17] pcH = −log [H$^+$].

[18] The value of pK_w for absolute ethanol is 19.1, according to G. Brierne, B. Crochon, and N. Felici, *C. R. Acad. Sci., Paris*, **254**, 4458 (1962).

[19] R. T. Kemp, Dissertation, University of Virginia, 1959.

[20] I. M. Kolthoff, *J. Phys. Chem.*, **35**, 2732 (1931).

[21] L. S. Guss and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **62**, 249 (1940).

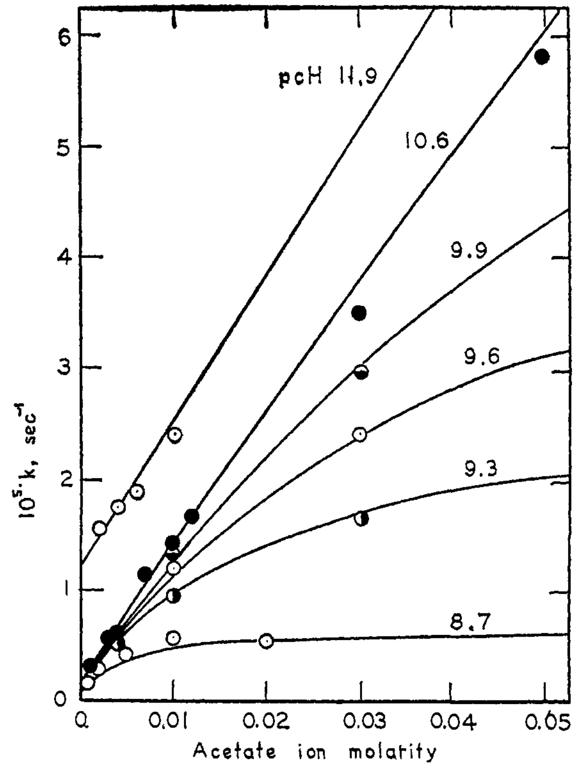


Figure 3. Family of curves calculated by eq 4 and experimental points showing pcH dependence of the acetate-catalyzed elimination.

No less important than the pcH-rate profile is the variation of rate with concentration of the acetate buffers, shown in Figure 3. Because specific salt effects are high in ethanol, no attempt was made to maintain constant ionic strength by adding electrolyte, except for the series at pcH 10.6, in which sodium chloride was added at the lower acetate concentrations, to rule out any sharp curvature or false catalytic effects due to electrolytes. Note that experiments at the same acetate ion concentration are strictly comparable in ionic strength since only the nonelectrolyte, acetic acid, is varied to change the pH. The effect of water (1%) or sodium chloride (0.01 *M*) on the rate at 0.01 *M* acetate ion concentration at pH 8.7 and 10.6 was shown to be negligible. Thus the spreading of the plots of *k vs.* [OAc$^-$] seems to be a function of reactant concentrations and can be interpreted as in the Discussion section.

Six kinetic runs with *threo*-SHCl in acetate buffers showed *k* values about 20 times as great as those of the *erythro* with similar hydrogen ion inhibition of the acetate catalysis.

Discussion

The data for the *erythro* substrate can be fitted to eq 4 by letting $k_1^{\text{EtOH}} = 8 \times 10^{-7}$ sec^{-1}, $k_1^{\text{EtO}^-} = 1.8 \times 10^2$ M^{-1} sec^{-1}, $k_1^{\text{OAc}^-} = 1.3 \times 10^{-3}$ M^{-1} sec^{-1}, and $k_2K_{\text{SHX}} = 1.5 \times 10^{-14}$ sec^{-1}. All the curves in Figures 1 and 3 are calculated from this equation.[22] The kinetics are therefore in accord with the two-step mechanism.

On the lower part of the pH-rate profile (Figure 1) the second term in the denominator in eq 4 is large and $k = k_2K_{\text{SHX}}/[\text{H}^+]$. This means that step 2 is rate controlling. Although the relatively high hydrogen ion concentration decreases the equilibrium concentration of SX$^-$, it also shortens the time required for step 1 to approach equilibrium.

When the pcH increases to 8, a plateau appears as the second term in the denominator of eq 4 becomes small in comparison with the first term. The ionization (1) then becomes rate controlling, and since the kinetically predominant base B is EtOH, the rate is independent of pcH, with $k = \Sigma k_1^{\text{B}}[\text{B}]$. Ethoxide ion begins to compete appreciably as the base B, around pcH 10, causing a steady increase in rate at higher pcH values.

There is no indication of the expected levelling off of the rate at very high pcH, as step 1 becomes rapid and complete, with step 2 again rate controlling, and the steady-state assumption is no longer valid. It would be of interest to observe this phenomenon. The rate of the dissociation 2 is not necessarily immeasurably fast, since there is considerable electronic rearrangement as the alkene S is formed. If K_{SHCl} were known, k_2 could be estimated since the steady-state treatment gives $k_2K_{\text{SHCl}} = 1.52 \times 10^{-14}$ M sec^{-1}. The constant K_{SHCl} cannot be measured but is estimated as follows. $k_{-1}^{\text{EtOH}_2^+}$, the rate constant for the recombination of oppositely charged ions, cannot be larger than about 10^{10} M^{-1} sec^{-1} (unless the solvated proton remains near the negatively charged carbon in an ion pair, in which case the recombination rate could be even higher).[23] In fact, it may be much lower in the case of an enolate ion. Since $k_1^{\text{EtOH}} = 8 \times 10^{-7}$ sec^{-1} for the ionization (eq 5), $K_{\text{SHCl}} = k_1/k_{-1} = 10^{-16}$ M. This lower limit may be compared with the following estimate: the dissociation constant of acetophenone[24] in water is about 10^{-16}. An α-chlorine atom increases the K_a of acetone by a factor of 3000 in water. If this inductive effect were not much different in methanol, K_{SHCl} in water would be 3×10^{-13}, without allowing for the effect of the β-chlorine. In ethanol, assuming the same medium effect as for acetic acid, K_{SHCl} would be decreased to about 10^{-19}. If $K_{\text{SHCl}} = 10^{-16}$, the calculated value of k_2, 1.5×10^2 sec^{-1}, is a specific dissociation rate for SHCl which would be easily measurable by flow methods.

$$\text{SHCl} + \text{EtOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{SCl}^- + \text{EtOH}_2^+ \qquad (5)$$

The spreading out of the curves in Figure 1 indicates a limitation of the effectiveness of general base catalysis at a given pcH. In terms of eq 3, lim $k = k_2K_{\text{SHX}}/[\text{H}^+]$. In mechanistic terms, when enough acetate ion is present to establish the equilibrium 1, additional quantities can do no more; hence at pcH 8.7, for example, k soon levels off. This amounts to the specific catalysis predicted for ElcB reactions with the first step at equilibrium.[25]

Although it is interesting to observe the kinetics of the rather rare ElcB mechanism, the results are not surprising; in fact the chalcone dichloride, SHCl, is one of the types which Ingold suggested would react in this way.[3] The presence of a carbonyl group introduces the possibility of acid-catalyzed steps but we can suggest none which would give rise to the kinetics and

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[22] For calculation of the pcH values, the pK_a of acetic acid in ethanol is assumed to be 10.6.

[23] W. J. Albery, *Progr. Reaction Kinetics*, **4**, 383 (1967).

[24] See ref 15, pp 105, 161.

[25] J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Amer. Chem. Soc.*, **78**, 3473 (1956).

logically give the observed products. It might be argued that the plateau in Figure 1, and the catalysis by buffers, are caused by acid-catalyzed *erythro* to *threo* conversion followed by the more rapid elimination of the latter form. This would explain the *trans* product. However, unless the *threo* substrate reacted by the ElcB mechanism, inhibition by hydrogen ion on the low-pH side of the plateau would still be unexplained for the *erythro* epimer.

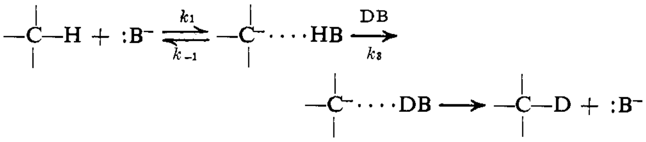
The relationship of rates and products to the configuration[1] of SHCl is entirely in accord with a previously published study of the chalcone dibromides.[26] At that time, lack of stereospecific elimination by the *erythro* form was attributed to the ElcB mechanism but the *threo* form, the conformation of which is probably correct for concerted elimination to *trans* product, was postulated to react by the E2 mechanism. If our brief kinetic study of *threo* SHCl is correct, both epimers eliminate *via* ElcB.

Interconversion of the epimers, through the enolate ion, might have been expected when step 1 is at equilibrium, which is true at low pcH (case A) or at pcH 8–10 with high buffer concentration (case B). However, recovery of the *erythro* isomer after 1 week in acidic ethanol, together with the absence of appreciable diminution of rate constant for the *threo* during the course of the reactions, indicated that such interconversion does not occur. Lutz[27] had already noted that the diastereoisomers of 1,2-dibenzoyl-1,2-dichloroethane were stable with respect to interconversion in acidic ethanol. We therefore assume that stereochemical and solvation effects cause the proton to return to the same side of the enolate ion that it left.

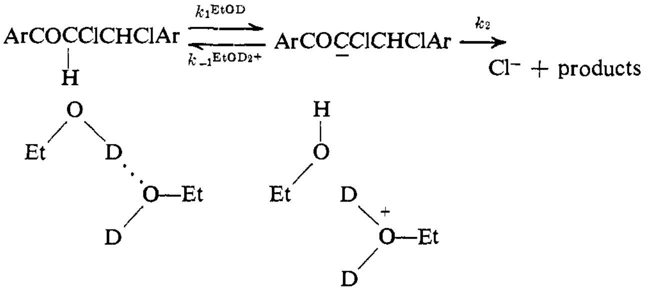
It appears, moreover, that if the assumption of a carbanion is correct, the same proton returns, because deuterium exchange in the substrate does not occur. Exchange was expected when k_{-1} was larger than k_2 (case A) or comparable to k_2 (case B). In the acetate buffer, 10% elimination took place in 5 hr, and 50% exchange of the H atom α to the carbonyl group was expected. In 10^{-5} *M* HCl in EtOD, substantial exchange was expected after 1 week. To the extent detectable by our nmr method, however, no exchange took place. These results are similar to the observations of Jones, Squires, and Lynn,[28] who found that although the rate of the piperidine-catalyzed elimination of a cyclohexyl tosylate was depressed by piperidinium ion, exchange was negligible.

We can formulate several possible causes of acid inhibition without exchange. An isotope effect, decreasing k_{-1} and thereby increasing the over-all rate of elimination, could account for the lack of exchange in case B. An inverse isotope effect was in fact observed, but its magnitude, $k_H/k_D = 0.8$ in 1 *M* CD_3COOD–0.01 *M* CH_3COONa, was too small to explain the results.

It therefore appears that if the ElcB mechanism is taking place, there must be a proton-transfer mechanism which, while returning the original proton to the carbanion, would be accelerated by increased hydrogen or deuterium ion concentration. Cram[29a] has described mechanisms elucidating the relationship between inversion and exchange in carbanions. He also has pointed out that the exchange of the carbon acid with a deuterated solvent may be slower than the ionization.[22b]



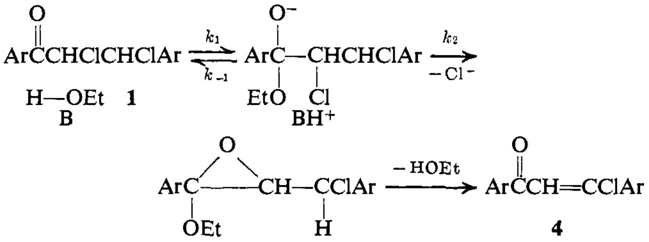
Possibly the value of k_{-1} can be increased by the action of protons through one or more solvent molecules to produce the observed kinetics even though HB has not diffused away, resulting in a kind of cage effect which makes exchange slow. The acetic acid molecule might also act as a bifunctional catalyst.



There is precedent for the repression of base-catalyzed exchange rate by hydrogen ions;[23] the exchange of ammonium salts in water, methanol, and ethanol shows this phenomenon.[30] Hine, on the other hand, found that the exchange of propionaldehyde was proportional only to the basic component of the buffer.[31] Exchange will be acid inhibited if the half-time for diffusion of the proton is longer than the lifetime of the carbanion (with respect to carbon protonation, not oxygen protonation to the enol). The average lifetime of our carbanions, the reciprocal of $k_2 + \Sigma k_{-1}^{BH}[BH^+]$, is rather short because if reprotonation does not take place, chloride ion is soon lost. However, the above-mentioned diffusion can be extremely rapid.[30c] Further discussion as to whether these mechanisms can account for acid inhibition without exchange in this elimination reaction must be postponed until measurable exchange is detected.

The carbonyl-addition mechanism shown in Scheme I, general base catalyzed like the hydration of acetal-

Scheme I



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(26) R. E. Lutz, D. F. Hinkley, and R. H. Jordan, *J. Amer. Chem. Soc.*, 73, 4647 (1951). It should be stated that the configurations of the various chalcone dihalides, including the diasteromeric pair used in this paper, are assigned on the strong and reasonable grounds of analogy, but that they are not rigorously established. It would be desirable to have absolute proof. However, even if these configurations had to be reversed, the data and general conclusions of this paper would not be vitiated.

(27) R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 1193 (1934).

(28) W. M. Jones, T. G. Squires, and M. Lynn, *ibid.*, **89**, 318 (1967).

(29) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965: (a) Chapter III; (b) p 28.

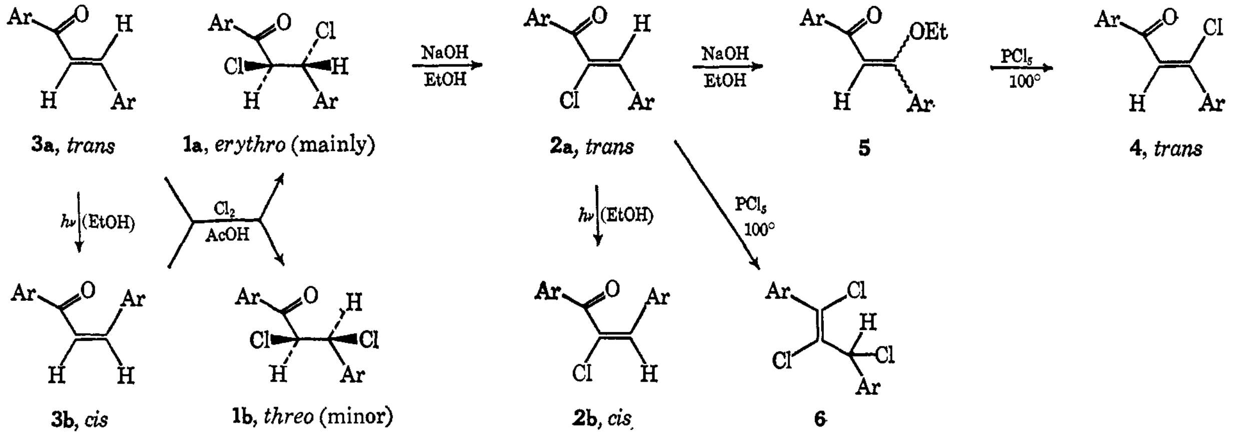
(30) (a) A. I. Brodskii and L. V. Sulima, *Dokl. Akad. Nauk SSSR*, **74**, 513 (1950); (b) C. G. Swain and M. M. Labes, *J. Amer. Chem. Soc.*, **79**, 1084, 1088 (1957); (c) E. Grunwald and M. Cocivera, *Discussions Faraday Soc.*, **39**, 105 (1965).

(31) J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Amer. Chem. Soc.*, **87**, 5050 (1965).

dehyde, would show the observed kinetics. However, the β-chlorochalcone **4**, prepared as described in the Experimental Section, was not a major product of the reaction. The other cases of acid inhibition of general base catalyzed elimination[14a,28] were moreover noted with substrates not containing carbonyl groups. Hudson and Klopman[14a] attributed the inhibition to interaction between acid and base, decreasing the activity coefficient of the base. Although it is true that the buffer solutions in which we found the greatest inhibition contained a high ratio of acetic acid to acetate ion so that this interaction was possible, there is no such simple explanation of the fact that the elimination proceeds slowly at pcH 6–8 but is practically halted by 10^{-5} *M* perchloric acid. However, the paper of Hudson and Klopman contains a very interesting piece of data: the greater the carbanion character of the E2 reaction, the greater is its sensitivity to acid. Evidently this subject requires further study.

Experimental Section[32]

The *cis* and *trans* isomers of 4,4′-dichlorochalcone, the *erythro*- and the *threo*-dichlorides, and the α- and β-monochloro derivatives were prepared by the methods shown in the chart relating compounds **1–6**, in which Ar is the *p*-chlorophenyl group.



trans-**4,4′-Dichlorochalcone**[33] **(3a)** produced yellow plates from ethanol, mp 157.5–159°, crystallizing from carbon tetrachloride as a polymorph, colorless needles, mp 154–155.5°. The polymorphs showed identical ir spectra which differed from those of the polymorphs of the *trans*-α-chloro derivative **2a**: $\lambda_{\max}^{\text{EtOH}}$ 228, 318 mμ (ε 13,200, 29,000); nmr, aromatic and vinyl multiplet, δ 7.22–8.09 ($CDCl_3$), 6.80–7.87 (C_6D_6).

1,3,4,6-Tetra-(4-chlorophenyl)hexa-1,6-dione (8). Reduction of **3a** by adding zinc to a refluxing acetic acid solution gave a 1:2 ratio of mono- and dimolecular product: the former, **7**, mp 83°;[33b] the latter, **8** (new), mp 252–254°, crystallized from acetone.

Anal. Calcd for $C_{30}H_{22}Cl_4O_2$ (**8**): C, 64.77; H, 3.99. Found: C, 63.31; H, 4.00.

cis-**4,4′-Dichlorochalcone (3b).** Sunlight irradiation of an ethanol solution of **3a** for 1 week gave a mixture consisting largely of **3b** (*cis*). Cooling first to room temperature gave a mixture of **3a** and **3b**; then cooling at −20° gave *cis* isomer **3b** as yellow plates, melting partially at 81° and changing to a colorless polymorph, mp 88–89.5°. The two polymorphs showed slightly different high-resolution ir spectra (CaF_2 prism, KBr pellets) with peaks at 7.04 and 7.22 μ for the yellow form only: $\lambda_{\max}^{\text{EtOH}}$ 264, 306 mμ (ε 15,800, 12,050); nmr, aromatic and vinyl multiplet, δ 6.5–7.9 ($CDCl_3$); AB quartet for 2 vinyl H, 6.00, 6.23, 6.38, 6.52; calcd $\nu_1 - \nu_2 = 14.1$ cps, $J = 14$ cps (C_6D_6).

Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.00; H, 3.64. Found for yellow form: C, 64.63; H, 3.14. Found for colorless form: C, 64.99; H, 3.55.

Approximate photoequilibration of the *cis–trans* isomers **3a** and **3b** under irradiation in ethanol at high dilution for 33 min, upon uv analysis, showed the *cis*/*trans* ratio to be about 10. Further irradiation gave progressively more of other products.

erythro- **and** *threo*-**4,4′-Dichlorochalcone Dichlorides (1a and 1b) (SHCl).** Chlorine was passed through a dispersion tube into a stirred suspension of 88 g (0.32 mol) of finely powdered *trans*-4,4′-dichlorochalcone (**3a**) in 250 ml of glacial acetic acid, as long as it was absorbed by the reaction mixture (10–15 min), during which time the dichloride precipitated. The reaction mixture was allowed to stand 1 hr, and the product was collected and washed repeatedly with pentane. The crude *erythro* product (**1a**, 57 g, mp 139.5–141.5°) was recrystallized from ethanol, mp 142–143.5°.[33b,34] Extensive manipulation of the residual oil gave another 3 g of **1a** (54% altogether) and 1.5 g (13%) of the *threo*-dichloride **1b**, mp 96–97.5°, crystallized from hexane. Also isolated and identified were the hydrolytic and cleavage products 4-chlorobenzoic acid (0.5 g) and 4-chlorophenacyl chloride (0.1 g). The residual 40 g of oil, with ir spectrum characteristic of the chalcone dichlorides,was column chromatographed over acid (Woelm) and basic (Fisher A-540) alumina, giving good yields of the *trans*-dehydrochlorination product **2b**.

Anal. Calcd for $C_{15}H_{10}Cl_4O$: C, 51.75; H, 2.89. Found for the *erythro* isomer **1a**: C, 51.84; H, 3.19. Found for the *threo* isomer **1b**: C, 51.82; H, 2.87.

The nmr spectrum for the *erythro* isomer **1a** showed the following: δ ($CDCl_3$), aromatic multiplet 7.4–8.11, 2 H singlet 5.42; δ (C_6D_6), AB quartet for 2 H, 5.04, 5.24, 5.32, 5.59; calcd $\nu_1 - \nu_2 = 16.2$ cps, $J = 10$ cps. The *threo* isomer was quite similar.

1,3-Di-(4-chlorophenyl)-3-acetoxy-2-chloropropanone (9). In another chlorine addition to **3a** as above, there was obtained 55% yield of *erythro* dichloride **1a**, no *threo* dichloride **1b**, and 3% acetoxy chloro addition compound **9**, mp 123–124.5°, crystallized from ethanol. The best yield of the last compound (15%), along with 3.5% of dehydrochlorination product **2a**, was obtained when sodium acetate was present in the reaction solution.

Anal. Calcd for $C_{17}H_{13}Cl_3O_3$: C, 54.91; H, 3.49. Found: C, 55.57; H, 3.86.

The nmr spectrum showed the following: δ ($CDCl_3$), 8 H aromatic multiplet 7.3–8.1, doublets 5.30 and 6.28 ($J = 9$ cps), CH_3 singlet 1.94.

1,3-Di-(4-chlorophenyl)-2-chloro-3-hydroxypropanone (10) was obtained by hydrolysis of 1 g of **9** by 50 ml of ethanol and 5 ml of concentrated hydrochloric acid (reflux 15 min); crystallization from hexane gave 55%, mp 103–105.5°.

Anal. Calcd for $C_{15}H_{11}Cl_3O_2$: C, 54.65; H, 3.36. Found: C, 54.49; H, 3.39.

trans-**4,4′,α-Trichlorochalcone (2a).**[19] A solution of 0.8 g (0.02 mol) of sodium hydroxide in 50 ml of ethanol was added dropwise over a period of 30 min to a stirred solution of 7 g (0.02 mol) of **1a** in 200 ml of ethanol (ice bath). Concentration on a steam bath under reduced pressure, followed by addition of water to incipient precipitation, gave 6 g (96%) of **2a**, recrystallized from ethanol, mp 56.5–57.5°. A polymorph was obtained from 95% ethanol and crystallized from benzene as colorless needles: mp 60–61.5°;

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(32) Melting points are corrected. Infrared spectra were taken on a Perkin-Elmer Model 21 spectrometer, nmr spectra on the Varian A-60 and, except for kinetic runs, ultraviolet spectra on the Beckman DK-2 spectrophotometer.

(33) (a) F. Straus and A. Ackermann, *Ber.*, 42, 1812 (1909); (b) H. O. House, *J. Amer. Chem. Soc.*, 78, 2298 (1956).

(34) J. A. Durden, Thesis, University of Mississippi, 1950, p 50.

nmr ($CDCl_3$), δ, aromatic and vinyl multiplet, 7.3–7.9; uv, $\lambda_{\max}^{\mathrm{EtOH}}$ 308 mμ (ε 21,500); ir, 6.07 μ (C=O).

Anal. Calcd for $C_{15}H_9Cl_3O$ (colorless polymorph): C, 58.0; H, 2.89. Found: C, 57.7; H, 3.14.

cis-**4,4′,α-Trichlorochalcone (2b).** Sunlight irradiation, for 1 week, of 500 ml of a 0.02 *M* ethanol solution of **2a**, after reported procedures for other chalcones and dypnones,[35] gave 1.6 g (52%) of **2b**, recrystallized from hexane: mp 99–101°; nmr ($CDCl_3$), δ, aromatic and vinyl multiplet 7.1–8.0; uv, $\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (ε 21,700); ir, 6.04 μ (C=O).

Anal. Calcd for $C_{15}H_9Cl_3O$: C, 58.0; H, 2.89. Found: C, 57.7; H, 3.11.

trans-**4,4′-Dichloro-β-ethoxychalcone (***trans***-1,3-Di-(4-phenyl)-3-ethoxypropenone) (5).** A solution of 3.1 g of **2a** in 100 ml of absolute ethanol and 0.4 g of sodium hydroxide was refluxed for 45 min, and 1.5 g (47%) of **5** crystallized on cooling, mp 92–96°.

Anal. Calcd for $C_{17}H_{14}Cl_2O_2$: C, 63.60; H, 4.37. Found: C, 62.51; H, 4.47.

Di(4-chlorobenzoyl)methane enol (11)[36] was isolated in a small amount from the filtrate from the above preparation of **5**, and it was obtained in 95% yield by hydrolysis of **5** (ethanol, concentrated HCl, refluxed 15 min), mp 162–163° (lit.[36] mp 158–159°), analyzed correctly for C, H; ir, 6.3 μ (no OH).

trans-**4,4′,β-Trichlorochalcone (1,3-Di(4-chlorophenyl)-3-chloropropenone) (4a).** A mixture of 3 g of **5** and 2 g of phosphorus pentachloride, melted over a steam bath and evaporated at reduced pressure with added hexane to remove phosphorus oxychloride, gave yellow crystals from methanol: mp 101.5–103.5°; nmr ($CDCl_3$), δ, aromatic and vinyl multiplet, 7.21–8.03; uv, $\lambda_{\max}^{\mathrm{EtOH}}$ 290 mμ (ε 17,000).

Anal. Calcd for $C_{15}H_9Cl_3O$: C, 58.00; H, 2.89. Found, C, 47.81; H, 2.93.

1,3-Di(4-chlorophenyl)-1,2,3-trichloropropene (6). A mixture of 3 g of **2a** and 2 g of phosphorus pentachloride was melted on a steam bath and dissolved in hexane. Evaporation on a steam bath under reduced pressure and treatment of the residual oil with methanol gave a 30% yield of colorless product, recrystallized from methanol: mp 113–113.5°; nmr ($CDCl_3$), δ, aromatic multiplet 7.25–7.47; H singlet 5.87.

Anal. Calcd for $C_{15}H_9Cl_5$: C, 49.15; H, 2.48. Found C, 48.96; H, 2.57.

Kinetic Procedure

The solvent was 99–100% ethanol, the water having been introduced with the buffer components. Reaction mixtures containing about 5×10^{-5} *M* SHCl and the requisite amount of hydrochloric acid, sodium ethoxide, or buffer were placed in the thermostat and analyzed without further dilution with a Beckman Model DU spectrophotometer. The following molar absorptivities were determined and used: at 262 mμ, SHCl 1.9×10^4 (max), *cis* S 2.35×10^4 (max), *trans* S 1.2×10^4; at 282 mμ, SHCl 5.8×10^3, *cis* and *trans* S 1.5×10^4 (isosbestic point); at 310 mμ, SHCl 1.5×10^2, *cis* S 4×10^3, *trans* S 2.15×10^4 (max). The values given for SHCl refer to *erythro*, but the spectrum of the *threo* is nearly identical. It is necessary to acidify ethanolic SHCl solutions with a trace of hydrochloric acid to prevent the appearance of elimination products in the spectrum.

In the samples from kinetic runs, the total concentration of S, *cis* and *trans*, was calculated from the reading at 282 mμ and the *cis*/*trans* ratio from that at 310 mμ. The solutions must be protected from strong sunlight or from prolonged exposure to ultraviolet radiation in the spectrophotometer to avoid interconversion of the *cis* and *trans* products. The previously reported[1] *trans*/*cis* ratio of about 2, in the products for *erythro* SHCl, was not observed in later experiments in opaque flasks. Although the over-all rates were reproducible, these experiments appeared to give approximately 100% *trans* product.

Detection of exchange in ethanol-d_1 was attempted with the following solutions in this solvent: (A) 0.01 *M* SHCl, 10^{-5} *M* HCl; (B) 0.01 *M* SHCl, 0.02 *M* CH_3COONa, 2.0 *M* CD_3COOD. After the desired time, the reaction mixtures were either evaporated until SHCl crystallized or added to 0.01 *M* sulfuric acid in H_2O (in one case, D_2O). The precipitate was collected, washed with water if acetate buffer had been used, dried (90% yield), and dissolved in benzene or $CDCl_3$ for nmr analysis at 60 Mc. The two nonaromatic protons of SHCl appear as one singlet, δ 5.4, in $CDCl_3$ but as the expected AB quartet centered at δ 5.3 in benzene.[37] The vinyl protons of the elimination products, *cis* and *trans*, appear with the aromatic protons. After each attempted exchange reaction, the area of the singlet in $CDCl_3$ still indicated approximately two protons and the shape of the quartet in benzene was unchanged. Just as significantly, the elimination rate constant showed no decrease throughout the course of the reaction, an isotope effect which exchange would almost surely have produced.

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(36) S. M. McElvain and K. H. Weber, *J. Amer. Chem. Soc.*, **63**, 2196 (1941).

(37) We are indebted to Mr. Andrew B. Turner and Mr. John R. Johnson for running nmr spectra and to Dr. D. W. Boykin for assistance in the interpretation. The nmr spectrum of chalcone dibromide has been discussed in detail by E. W. Garbisch, Jr., *J. Chem. Educ.*, **45**, 320 (1968).