[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Displacement Reaction of Haloalkenes with Iodide Ion. A Survey of Reactivity and Mechanism[1]

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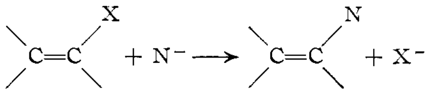
The halide exchange of twelve chloro- or bromoalkenes with iodide ion proceeds to a measurable extent in the range 148–200°. In the reaction of iodide with *cis*- or *trans*-*p*-nitro-ω-bromostyrene in diethylene glycol mono-*n*-butyl ether, the exchange rates are greater than the isomerization rates. A mechanism has been suggested to accommodate these facts.

It has been known for a long time that nucleophilic displacement at unsaturated carbon atoms, aromatic,[2] acetylenic[3] and ethylenic,[4] is difficult. For aryl compounds there is an abundant and excellent literature to illustrate and qualify this remark.[2] In contrast, few systematic data are available on the other unsaturated systems. For example, previous attempts to effect direct substitution of an acetylenic halogen appear to have been unsuccessful.[3,4c] Until recently there has been little reliable information on the displacement of ethylenic halogens. In this work we report on the reactivity of several haloalkenes toward iodide ion and propose a mechanism for such displacements.[5]

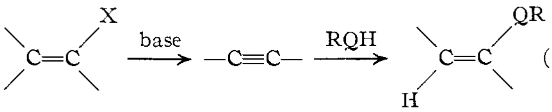
The reaction of interest is of the type



$$\mathrm{>C{=}}\overset{X}{\mathrm{C}}\mathrm{<} + N^- \longrightarrow \mathrm{>C{=}}\overset{N}{\mathrm{C}}\mathrm{<} + X^- \qquad (1)$$

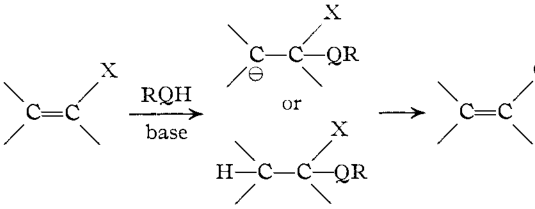
It has not always been recognized that (1) may be the over-all result of a series of reactions. There is, however, a growing body of work which is especially revealing in showing the alternative paths by which the product may be formed.[7-10] Clearly differing from single-stage displacement, these paths can be summarized:

elimination addition[11,12]



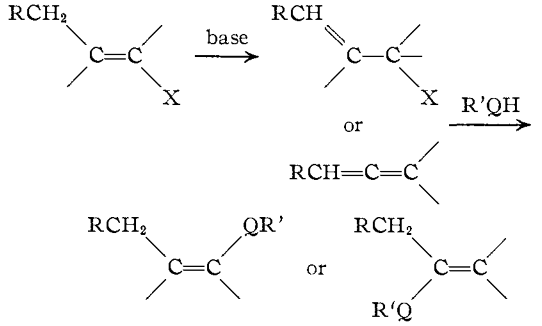
(2)

addition–elimination[9,13]



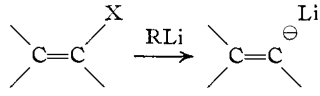
(3)

allylic rearrangement[8] or allenic intermediate[6,14]



(4)

ethylenide intermediate[15]



(5)

Evidently, questions such as concerted backside displacement or non-stereospecific displacement for process (1) can be discussed in a given case only after the above possibilities have been recognized.[16-19]

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[1] This work was supported by Research Corporation.

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[4] (a) H. A. Smith and W. H. King, THIS JOURNAL, **72**, 95 (1950); (b) L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948); L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949); G. Salomon and A. J. Ultee, *Rec. trav. chim.*, **69**, 95 (1950); A. J. Ultee, *ibid.*, **68**, 125 (1949); P. Petrenko-Kritschenko, *Ber.*, **62**, 581 (1929); (c) J. Loevenich, J. Losen and A. Dierichs, *ibid.*, **60**, 950 (1927); (d) A. Juvala, *ibid.*, **63**, 1989 (1930).

[5] These data as well as unpublished data on the reaction of phenylbromoacetylene with iodide suggest the following reactivity order: allenic[6] > acetylenic > ethylenic > aromatic.[2c]

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[16] C. S. Marvel in "Organic Chemistry," Vol. I, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 455; A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933).

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[19] It is probable that the elimination–addition sequence applies in the systems: trichloroethylene, ethoxide[20]; 1- or 2-chloropropene or 1,2- or 1,1-dichloropropene, ethoxide[4a]; 1,2-dibromoethene, phenoxide[14b]; 1,2-diiodoethene, cyanide[21]; β-chlorostyrene, ethoxide[22];

In what are probably the most important reports on the mechanism of nucleophilic displacement at an alkene carbon, it appears that exchange with retention of configuration may be the main process.[10] For example, Jones and Vernon find that the reactions of alkoxide with the ethyl β-chlorocrotonates "proceed largely though not completely with retention of configuration."[10a] Similarly, the *cis*- and *trans*-aryl-selenoacrylic acids can be made from the *cis*- and *trans*-chloroacrylic acids, respectively.[10b]

To avoid the complication inherent in a system containing strong base and haloalkene, we studied reactions of the type

$$\mathrm{R_1R_2C{=}CR_3X + I^- \longrightarrow R_1R_2C{=}CR_3I + X^-} \quad (6)$$
$$\mathrm{X = Cl,\ Br}$$

The first portion of the work was exploratory in the sense that a rapid survey of reactivity was made. No special efforts were made to separate *cis–trans* mixtures. In this survey, a suitable *cis–trans* pair, the *p*-nitro-ω-bromostyrenes, was found for more detailed study. Kinetic data as well as product analyses suggested a general mechanism for process 6.

Experimental

Materials.—Butanol–water and a glycol monoether were used as solvents. The butanol gave negative tests for halide with silver nitrate, for aldehyde with Tollens reagent and for peroxides with ferrous thiocyanate or sodium iodide. Commercially available diethylene glycol mono-*n*-butyl ether (Butyl Cellosolve) gave negative halide and aldehyde tests but positive peroxide tests. Activated alumina removed only some of the peroxides. Therefore, the glycol ether was refluxed for several hours with a mixture of ferrous sulfate and potassium bisulfate and distilled under reduced pressure. The middle cuts, b.p. 69–70° at 0.3 mm. or 73–74° at 0.5 mm. (lit.[26a] b.p. 70° at 1 mm.), $n^{20}\mathrm{D}$ 1.4286 (lit.[26b] $n^{20}\mathrm{D}$ 1.4321) were used. No peroxide could be detected after this treatment.

The following substances were purified by fractional distillation, usually from a few crystals of diphenylamine: 1,2-dibromoethene, b.p. 34° at 37–38 mm., $n^{25}\mathrm{D}$ 1.5340 (lit.[27] *cis*, $n^{20}\mathrm{D}$ 1.5370; *trans*, $n^{25}\mathrm{D}$ 1.5440); 1-bromo-1-butene, b.p. 29° at 5 mm., $n^{20}\mathrm{D}$ 1.4575 (lit.[28] *cis*, $n^{18.5}\mathrm{D}$ 1.4555; *trans*, $n^{16.2}\mathrm{D}$ 1.4600); 2-bromo-1-butene, b.p. 25° at 10 mm., $n^{20}\mathrm{D}$ 1.4540 (lit.[28] $n^{18.7}\mathrm{D}$ 1.4523); 2-bromo-2-butene, b.p. 30° at 60 mm., $n^{20}\mathrm{D}$ 1.4598 (lit.[28] *cis*, $n^{19.1}\mathrm{D}$ 1.4631; *trans*, $n^{16.3}\mathrm{D}$ 1.4602), β-bromostyrene, b.p. 61° at 1' mm., $n^{20}\mathrm{D}$ 1.6081 (lit.[11] *cis*, $n^{20}\mathrm{D}$ 1.6007; *trans*, $n^{20}\mathrm{D}$ 1.6100).

The gases, vinyl bromide and chlorotrifluoroethene, were passed from their cylinders into the solvent without further purification. Hexafluoro-2,3-dichloro-2-butene, $n^{26}\mathrm{D}$ 1.3438 (lit.[29] $n^{20}\mathrm{D}$ 1.3459) and 3,3-difluoro-1,2-dichloro-1-propene, $n^{26.8}\mathrm{D}$ 1.4150 (lit.[30] $n^{20}\mathrm{D}$ 1.4152) were commercial materials.

ω-Bromopentachlorostyrene was prepared by the method of Ross, *et al.*,[18] m.p. 113–114° (lit.[18] 113–115°). *cis* and *trans* *p*-nitro-ω-bromostyrene were prepared by the method of Cristol and Norris[11]; for *trans*, m.p. 159.5–160° (lit.[11] 156–157°); for *cis*, m.p. 47–48° (lit.[11] 49°).

Analytical Methods.—Several concentrations of silver nitrate, 0.02–0.1 *N*, were used to estimate the inorganic halides. An amperometric method involving the Sargent Ampot was used for the analyses. By this method one determines the iodide in an ammoniacal medium, then chloride or bromide in a solution containing nitric acid.[31] In order to avoid halide contamination during the titration, a short glass leg fitted with a coarse fritted glass disk and containing a gel of 3% agar, 30% ammonium nitrate was interposed between the potassium chloride salt bridge and the solution to be analyzed.

The accuracy of the amperometric method was checked both against known weights of the alkali halides and against the adsorption indicator titration when this was possible. The accuracy attainable was satisfactory: for example, a solution made up to contain 0.1001 mmole of chloride and 2.597 mmoles of iodide analyzed 0.098 mmole of chloride and 2.606 mmoles of iodide. Similarly, a solution containing 0.1001 mmole of bromide and 2.597 mmoles of iodide analyzed 0.106 mmole of bromide and 2.588 mmoles of iodide.

In the exchange studies both halide ions were always determined. With *cis*-*p*-nitro-ω-bromostyrene difficulties in the analytical method turned up. Since the iodide was estimated in ammonia solution containing *ca.* 10^{-3} *N* hydroxide ion, it appeared that the reaction

$$p\text{-}\mathrm{O_2NC_6H_4CH{=}CHX + OH^- \longrightarrow}$$
$$p\text{-}\mathrm{O_2NC_6H_4C{\equiv}CH + X^- + H_2O} \quad (7)$$

was taking place during the 10–15 min. period of the titration.[32]

To reduce the side reaction, the solution to be analyzed was jacketed before and during titration with an ice slush. The time during which hydroxide was present was cut to 5–8 min. The error arising from (7) was now in the range of the other experimental errors.

Exchange Experiments.—The sealed ampule technique was used. The ampules were flushed with nitrogen before and after the aliquot of solution was added and then sealed. The thermostats were an oil-bath and a Carius furnace for the survey work and a fused salt-bath[33] for the kinetic study. The thermometers of the salt bath were calibrated against a platinum resistance thermometer; the uncertainty in the temperature here was ±0.1° and the uncertainty in the reaction time for a given ampule was ±2 min. The corrections that were applied to the rate constants because of the expansion of the diethylene glycol mono-*n*-butyl ether were found to be 1.158, 1.191 and 1.230 at 174.1, 196.0 and 222.2°, respectively.

Results

Preliminary Exchange Studies.—A survey of the haloalkene reactions with iodide ion is given in Table I. The per cent. exchange was calculated from the ratio of the inorganic iodide which had disappeared to the initial iodide concentration. The per cent. excess halide was calculated from the ratio of the amount of all inorganic halide in excess of initial iodide to the initial iodide concentration. Although efforts were made to purify the starting materials, it is possible that a haloalkene, sensitive perhaps to traces of oxygen or iodine, would give

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ω-chloro or bromopentachlorostyrene, ethoxide[18]; vinyl bromide or α-bromoheptene, ethyl mercaptide.[4c] It is probable that the addition–elimination sequence applies to the systems α- or β-bromoacrylic acids or α- or β-chlorocrotonic acids, arsenite[23]; tetrachloroethene, thiophenoxide[24]; chlorovinyl sulfones or chlorovinyl sulfides, various nucleophiles.[9,25]

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(30) M. Hauptschein and L. A. Bigelow, *ibid.*, **73**, 1428 (1951).

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(32) For the elimination reaction of the *cis*- and *trans*-bromides the rate constants at 25° are 0.6 and 3 × 10^{-6} l. mole^{-1} sec.$^{-1}$, respectively.[11]

(33) W. E. Kirst, W. M. Nagle and J. B. Castner, *Chem. Met. Eng.*, **47**, 42 (1940).

TABLE I

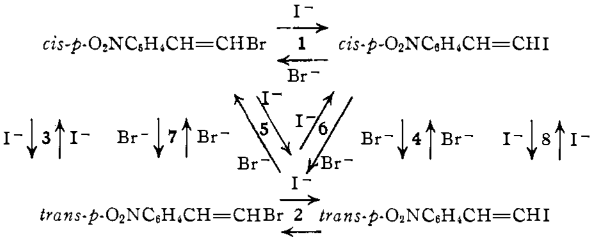
EXCHANGE REACTION OF HALOALKENES WITH IODIDE ION IN BUTANOL–WATER[a]

Haloalkene[b,c]	Hr. ±0.5 at 148 ± 5°	Exchange, %	Hr. ±0.5 at 200 ± 5°	Exchange,[34] %
$H_2C{=}CHBr$	166	1	91	3.8
a = 0.135	320	1.4	166	5.4
b = .1005	436	1.4	320	16.1 (3.6)[c]
$C_2H_5CH{=}CHBr$	173	3.2	72	6.7
a = 0.1004	341	3.6	166	13.5
b = .1010	584	5.2	268	36.8 (2.4)
$C_2H_5CBr{=}CH_2$	127	1.2	88	6.3
a = 0.1004	152	1.2	187	6.5
b = .1002	489	3.8	346	48 (8)
$CH_3CBr{=}CHCH_3$	164	3.2	73	13.6
a = 0.0997	330	4.5	163	26.8
b = .1003	484	6.4	307	41
$CHBr{=}CHBr$	67	4.1	48	45.2
a = 0.0995	137	5.3	137	51.7 (2.2)
b = .1015	327	9.2	215	45.5 (1.8)
$C_6H_5CH{=}CHBr$	95	1.7	64	23.8
a = 0.0928	165	1.8	132	21.6
b = .0988	316	2.2		
cis-*p*-$NO_2C_6H_4CH{=}CHBr$[d]	2.98[e]	10.5	1.53[f]	19.2
a = 0.1204	6.53	20.1	3.95	36.5
b = .0834	9.98	27.6	7.63	52.1
trans-*p*-$NO_2C_6H_4CH{=}CHBr$[d]	2.00[f]	3.85	1.08[g]	10.0
a = 0.0254	3.90	6.92	3.03	20.7
b = .0507	6.05	10.3	6.97	32.7
$C_6Cl_5CH{=}CHBr$[h]			90	14.5
a = 0.0234			140	26.0
b = .0500			189	29.2
			282	33.4
$HCF_2CCl{=}CClH$	73	8.5	49	11.9
a = 0.1005	145	8.7	145	14.5
b = .1002	219	9.4 (1.4)	194	18.4
$CF_3CCl{=}CClCF_3$	28	2.0	50	6.3
a = 0.0999	113	3.1	95	24.6
b = .1064	360	4.9	208	36.6 (3.1)
			329	35.8 (11.5)
$CF_2{=}CFCl$	24	14.7	26	24.0
a = 0.1030	65	18.4	47	27.1
b = .1428	88	24.7	70	25.2

[a] Eight per cent. water by volume. [b] *a* = concentration in moles/liter of haloalkene, *b* = concentration in moles/liter of either sodium or potassium iodide. [c] Per cent. excess halide in parentheses. [d] The solvent was ethylene glycol mono-*n*-butyl ether. [e] Run at 174°. [f] Run at 196°. [g] Run at 222°. [h] Exchange with Cl cannot be excluded.

erratic results; for example, see the data for 1,2-dibromoethene at 200°. In fact, in preliminary work in which various solvents were tested and/or in which the alkene may have been impure, several explosions occurred. The system ω-bromostyrene in ethylene glycol at 200° was such a case. The occasional presence of excess inorganic halide was noted most often in long-term ampules; visible decomposition of organic halide was also in evidence. Another possible source of excess halide, the reaction between the haloalkene and the basic medium in which the analyses for iodide were made, was considered to be far less important.

Product Analyses.—The exchange of iodide with *p*-nitro-ω-bromostyrene was studied in detail in the solvent diethylene glycol mono-*n*-butyl ether. The following set of reactions must be considered.



(8)

Any one compound could lead to all four. Since the organic iodides were not known, an indirect method of product analysis was developed.

It is well known that the base-catalyzed elimination from a haloalkene is favored when the leaving groups are *trans*.[11,12a] For the pair *cis*- and *trans*-*p*-nitro-ω-bromostyrene the rate ratio of dehydrobromination with base at 43° is *ca.* 1.6 × 10⁴. Thus, it was possible to decompose the *cis* isomers selectively and estimate their concentrations from the halide produced.

Two ampules of a given run were kept at the same temperature for the same period of time. One was analyzed by the usual method. The contents of the other were treated with sodium hydroxide in 2-propanol at 0° for 30 min. or at 25° for 20 min. (> 95% elimination). The mixture was acidified with glacial acetic acid and then analyzed in the usual way for both halides—fortunately the *p*-nitrophenylacetylene did not interfere. Since initial concentrations of *cis*- or *trans*-bromide and of sodium iodide were known, analysis of the first ampule gave the concentrations of sodium iodide, sodium bromide, total organic iodide and total organic bromide. Analysis of the second ampule gave both the increase in sodium iodide or the *cis* iodide concentration and the increase in sodium bromide or the *cis* bromide concentration. The *trans* compounds could now be obtained by difference. The results of such experiments are given in Tables II and III. Because of thermal decomposition of the organic halides and because of reaction 7, these data are only approximate: the uncertainty in the *cis* and *trans* compositions may be as high as 3 mmoles/l. (see next section).

TABLE II

PRODUCT ANALYSIS FOR THE REACTION OF *cis*-*p*-NITRO-ω-BROMOSTYRENE WITH SODIUM IODIDE AT 196°: MMOLE/L.

a = 0.0773, *b* = 0.1050

Time, hr.	Organic bromide	*cis*-Bromide	*trans*-Bromide	Organic iodide	*cis*-Iodide	*trans*-Iodide
10.77	33	21	12	44	25	19
16.20	27	6	21	50	29	21
32.34	22	1	21	55	19	36
54.60	21	4	17	56	20	36
95.30	20	1	19	57	9	48

TABLE III

PRODUCT ANALYSIS FOR THE REACTION OF *trans*-*p*-NITRO-ω-BROMOSTYRENE WITH SODIUM IODIDE AT 196°: MMOLE/L.

a = 0.0649, *b* = 0.1050

Time, hr.	Organic bromide	*cis*-Bromide	*trans*-Bromide	Organic iodide	*cis*-Iodide	*trans*-Iodide
18.87	29	1	28	36	0	36
30.38	24	2	22	41	1	40
96.60	18	4	14	48	4	44

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(34) In the light of the data it would appear that the rate constants reported for the exchange at 15° of vinyl bromide and 1-bromopropene with potassium iodide are far too large.[4d]

Since they are drawn from the same run, the data in Tables II, IV and Fig. 1 for the reaction of *cis-p*-nitro-ω-bromostyrene with sodium iodide at 196° may be compared in detail. It is seen that at equilibrium *ca.* 75% of the organic halide is present as iodide and this is chiefly *trans*. At *ca.* 57% organic iodide, however, *cis* isomers still predominate. Similar analyses for a *cis* run at 174° indicate that the *cis* compounds persist even longer relative to the per cent. exchange. It is clear that the halide exchange of *cis-p*-nitro-ω-bromostyrene with sodium iodide proceeds primarily with retention, but that isomerization becomes increasingly important as equilibrium is approached.

TABLE IV

THE KINETICS OF REACTION BETWEEN *cis-p*-NITRO-ω-BROMOSTYRENE AND SODIUM IODIDE AT 196.0 ± 0.1° IN DIETHYLENE GLYCOL MONO-*n*-BUTYL ETHER

$a = 0.0773$, $b = 0.1050$

Time hr.	x mole/l.	k l. mole^{-1} hr.$^{-1}$
1.27	0.0106	1.19
2.02	.0151	1.12
2.78	.0196	1.13
3.55	.0248	1.21
5.06	.0297	1.12
6.92	.0361	1.14
10.77	.0444	1.14
16.20	.0502	1.10
32.34	.0545	..
54.60	.0560	..
71.13	.0570	"Equilibrium"
95.30	.0574	"Equilibrium"
117.00	.0574	"Equilibrium"

In the reaction of *trans-p*-nitro-ω-bromostyrene with sodium iodide at 196° the exchange with retention appears to be more decisive. This is, of course, a consequence of the greater stability of the *trans* isomers.

Kinetic Study.—Early in the work, it was observed that the reactions of haloalkenes with iodide ion appeared to be reversible. Despite the fact that it was not possible to start with the iodo compounds and bromide ion, the evidence for an equilibrium in (8) was unambiguous. At constant total inorganic halide concentration the per cent. exchange eventually levelled off (see Fig. 1). Starting with different concentrations of either organic bromide and sodium iodide one could calculate a "constant," the equilibrium constant.

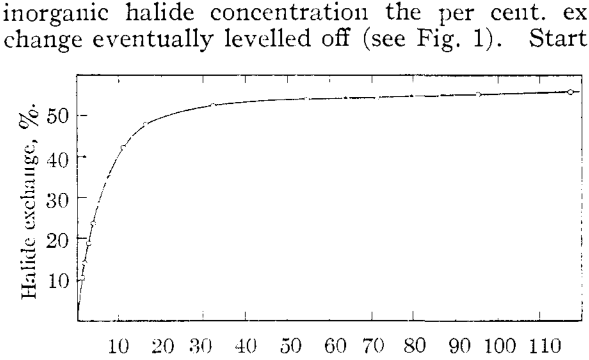

Fig. 1.—Iodide ion exchange with *cis-p*-nitro-ω-bromostyrene at 196° (a = 0.0773, b = 0.1050).

For the kinetics the expression

$$dx/dt = k_f(a - x)(b - x) - k_b x^2 \qquad (9)$$

was integrated to give

$$k_f = \frac{2.303}{mt} \log \frac{\left[\frac{K(a + b + m)}{2(K - 1)} - x\right](a + b - m)}{\left[\frac{K(a + b - m)}{2(K - 1)} - x\right](a + b + m)} \qquad (10)$$

where

$$m = \sqrt{(a + b)^2 - 4ab(K - 1)/K} \qquad (11)$$

and

$K = k_f/k_b$, $K_1 = k_1/k_{-1}$, etc., in which the k's refer to processes in (8) (12)

b = concn. of iodide ion, moles/l.

a = concn. of *cis-* or *trans-p*-nitro-ω-bromostyrene, moles/l.

x = concn. of *cis-* or *trans-p*-nitro-ω-iodostyrene, moles/l. at time t

t = time in hours

k_f = rate constant for the forward reaction

k_b = rate constant for the reverse reaction

To evaluate K, x was estimated graphically from a plot of per cent. reaction *versus* time (see Fig. 1). Extrapolation to "infinite" time from points close to equilibrium was necessary because of difficulties with long term ampules. After several hours the contents of an ampule would begin to darken. In the early ampules the total halide concentration was unaffected. Near equilibrium, however, the ampules were opaque and an excess of inorganic halide was found; a black deposit, soluble with difficulty in nitric acid and containing halogen, was formed. Thus, very little useful information could be obtained from the "infinity" ampules.

In passing, it might be mentioned that several attempts to obtain K_3 from equilibration of the *p*-nitro-ω-bromostyrenes with bromide ion were unsuccessful. Since longer reaction times with bromide ion as compared with iodide ion appeared to be necessary, there was even greater decomposition of the organic compounds.

As determined here, the meaning of k_f and K requires clarification. To obtain rate constants for the *cis* and *trans* bromides, it was assumed that only process **1** or **2** of (8) need be considered. At equilibrium, however, all four compounds were present. It is clear that K = (total organic iodide)(Br$^-$)/(total organic bromide)(I$^-$). At 196° this ratio is constant, as it should be according to (8), whether *cis-* or *trans*-bromide is the starting material. The assumption that K approximates K_1 and K_2 requires the plausible equality (*cis*-iodide/*cis*-bromide) = (*trans*-iodide/*trans*-bromide). Fortunately the rate constants were usually relatively insensitive to even a 15–20% variation in K.

Table IV and Figs. 2 and 3 show typical data at 196°. The rate constants were calculated from the slopes of the kt *vs.* t plots, then corrected to k_{cor} for the expansion of solvent. All of the data are summarized in Table V. The parameters of the expression[35]

$$k_{cor} = \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \qquad (13)$$

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(35) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 196.

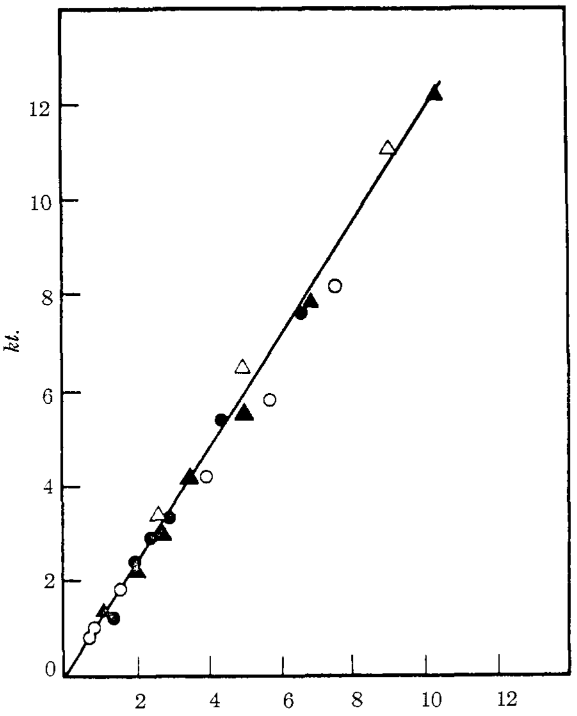

Fig. 2.—Iodide ion exchange with *cis*-*p*-nitro-ω-bromostyrene at 196.0 ± 0.1° (four runs).

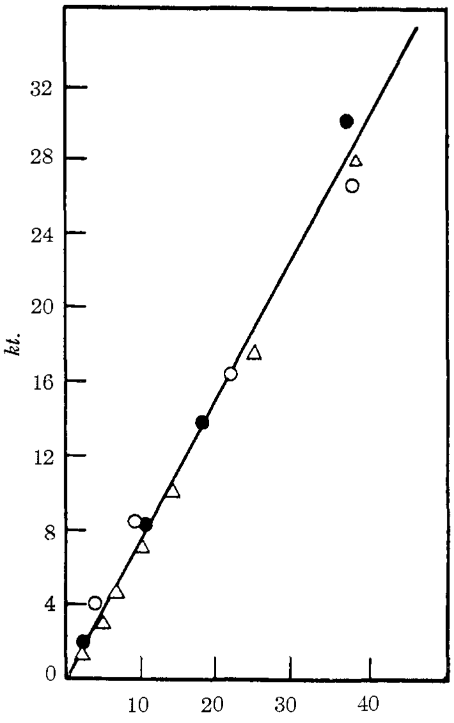

Fig. 3.—Iodide ion exchange with *trans*-*p*-nitro-ω-bromostyrene at 196.0 ± 0.1° (three runs).

are also given. Since the data at 222° were limited, the values for the activation parameters of *trans* *p*-nitro-ω-bromostyrene are somewhat uncertain.[36]

TABLE V

RATE DATA FOR THE REACTION OF *p*-NITRO-ω-BROMOSTYRENES WITH SODIUM IODIDE IN DIETHYLENE GLYCOL MONO-*n*-BUTYL ETHER

cis, mole/l.	NaI, mole/l.	Temp., °C.	$k \times 10^4$, l./mole sec.	K
0.1204	0.0834	174.1 ± 0.1	1.04 ± 0.05	2.8 ± 0.2
.0996	.1237			
.1008	.1288			
.1204	.0834	196.0 ± 0.1	3.83 ± 0.19	3.4 ± 0.3
.0996	.1237			
.0515	.0561			
.0773	.1050			
$\Delta H^{\ddagger} = 23.9 \pm 1.3$ kcal./mole, $\Delta S^{\ddagger} = -24 \pm 5$ cal./mole deg.				
trans				
0.0436	.0508	196.0 ± 0.1	2.58 ± 0.09	3.1 ± 0.3
.0437	.1020			
.0254	.0507			
.0254	.0507	222.2 ± 0.1	1.33 ± 0.9	4.2 ± 0.5
.0809	.1116			
$\Delta H^{\ddagger} = 27.9 \pm 1.3$ kcal./mole, $\Delta S^{\ddagger} = -16 \pm 5$ cal./mole deg.				

Discussion

The data in Table I confirm the notion that haloalkenes are less reactive than haloalkanes in displacement reactions. Since (6) is apparently an equilibrium reaction, the per cent. exchange should not, however, be interpreted as an approximate reactivity order.

The introduction of electron-withdrawing groups such as *p*-nitrophenyl, pentachlorophenyl, fluoro and trifluoromethyl groups clearly increases the reactivity of the haloalkene. This has of course been demonstrated elsewhere in the reactions of halovinyl ketones,[13] acid derivatives,[10] sulfides and sulfones.[9] The nature of the substituents suggests that both resonance and inductive assistance can increase the reactivity of the haloalkene.

Concerning the mechanism of displacement at an ethylenic carbon atom, our point of view derives largely from the earlier contributions of Gold,[17] Bunnett and Zahler,[2a] and Noyes, *et al.*[37]: in detail it may be identical with the view taken by Jones and Vernon.[10a] Based on the reaction of iodide ion with the *p*-nitro-ω-bromostyrenes such a mechanism must be consistent with the following observations: (1) in the early stages the reaction proceeds largely with retention of configuration, (2) all four geometrical isomers are present at equilibrium, (3) the rates of formation of the

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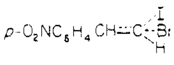
[36] Dr. R. M. Noyes has suggested that our data might yield further crude but detailed information on the interesting scheme given by (8). Concentration *versus* time plots were made for each of the organic compounds in the runs of Tables II and III. Rate constants were estimated from the initial slopes of these curves. The measured constants, for example $k_f \doteq k_1 + k_5$ in the case of the *cis* bromide, were used to guide these estimates. From the *cis* data we obtained $k_1 \simeq 3.2$ and $k_3 \simeq 0.5$, $k_5 \simeq 0.6$ and from the *trans* data $k_2 \simeq 2.6$ and $k_{-3} \simeq k_6 \simeq 0.02$. The ratio k_3/k_{-3} gives $K_3 \simeq 25$. In the *trans* run it appeared that the *trans* isomers were essentially equilibrated before any appreciable quantities of the *cis* isomers were present. Hence it follows that $K \simeq K_1 \simeq K_2 \simeq 3$, $K_4 \simeq 25$, $K_5 \simeq 75$, $K_6 \simeq 0.12$, $k_{-5} \simeq 0.0008$ and $k_{-6} \simeq 0.0003$. Liter mole^{-1} sec.$^{-1}$ $\times 10^{-4}$ are the units for all of the above rate constants.

[37] R. M. Noyes, R. G. Dickinson and V. Schomaker, THIS JOURNAL, **67**, 1319 (1945); H. Steinmetz and R. M. Noyes, *ibid.*, **74**, 4141 (1952).

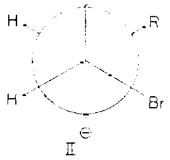
trans iodide and bromide from the *cis* bromide are roughly the same and the rates of formation of the *cis* isomers from the *trans* bromide are also similar.

It is suggested that the following mechanism accords with the facts. For concreteness, iodide ion and *cis*-*p*-nitro-ω-bromostyrene are chosen as reactants. The iodide attacks along a line perpendicular to the plane of the alkene by an interaction with the pi orbital. The activated complex may be represented by I. By losing bromide or iodide ion, the complex can return to its original configuration; alternatively, by losing its double bond completely it can yield the intermediate II. (The structure of the activated complex needs no more specification than to say that it is a stage in the formation of II.) II is pictured in the Newman notation[38]: all of the bond angles are close to tetrahedral, R is the *p*-nitrophenyl group and the electron pair is on the carbon adjacent to the reaction site. This might be named "concerted" process 1.

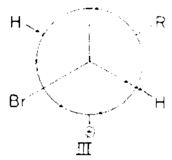


$p\text{-}O_2NC_6H_4CH{=}\overset{I}{\underset{H}{C}}{\cdots}Br$

I



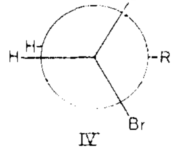
II



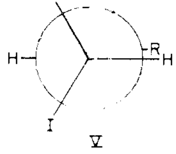
III

To bring in a possible stepwise process for halide exchange with retention as well as to account for isomerization, we consider the isomers of II. II is one of a pair of D- and L-forms; it is also one of a set of three *threo* rotamers. Carbanion III is one of the diastereoisomeric set of *erythro* rotamers. Rotational barriers of 3–5 kcal. separate the members of each set.[39] The *threo* and *erythro* isomers are separated by a barrier to inversion at the carbon atom adjacent to the reaction site. Because the negative charge on these carbanions is distributed at least partially on the *p*-nitrophenyl group, the inversion barrier at the carbon atom adjacent to the reaction site is probably less than 7 kcal., a figure calculated for tetrahedral CH_3^-.[40] Finally, it is assumed that halide will depart only when it is *trans* to the electron pair in any isomer of II.

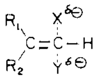
If inversion is faster than internal rotation, then the groups attached to the carbon atom adjacent to the reaction site are coplanar (on the average) and only IV and V need be considered. In this situation exchange with retention is favored and isomerization results simply from internal rotation between IV and V. This case might be called "stepwise" process 2 and is independently consistent with the data.



IV



V



$\begin{matrix} R_1 & & X^{\delta\ominus} \\ & C{=}C{-}H & \\ R_2 & & Y^{\delta\ominus} \end{matrix}$

VI

If inversion is slower than internal rotation, the route from *cis* to *trans* may be tortuous. Of the six rotamers, it appears that II and III would be formed most readily from the *cis* and *trans* bromides, respectively, since their formation involves a minimum of reorganization of the groups on the alkene carbons. If the iodine atom and the electron pair enter *trans* in the plane of the original pi orbital, then each of these groups moves only 30 degrees (in projection). Now II and III are not interconvertible by rotation. Then if they lie on the path of lowest energy from *cis* to *trans*, both inversion at the carbon adjacent to the reaction site and internal rotation will be necessary for *cis*–*trans* isomerization. This might be called stepwise process 3 and must be slower than exchange with retention by other paths.

The preceding discussion has perhaps indicated the problems associated with the assignment of a mechanism. With other assumptions, the number of plausible paths increases. However, the general scheme

cis-isomers $\rightleftarrows$ "*cis*" carbanion $\rightleftarrows$
"*trans*" carbanion $\rightleftarrows$ *trans*-isomers

appears to cover the possibilities and to account for the experimental results.[41]

Although the experimental data almost exclude mechanisms which invert the carbon at the reaction site, it is instructive to examine them. It has already been suggested that tetrahedral rotamers which lead to inversion are on high energy paths. The planar activated complex VI has been postulated more often as the logical analog of the SN2 complex of an alkyl halide: X^- presumably approaches in the plane of the molecule and, as Y^- departs, begins to bond at the smaller lobe of the sp^2 orbital of the carbon–halogen bond. At the reaction site the bond angles are 90°, the CX and CY bonds are each p/2 and the carbon hydrogen bond is sp.[16,17] A scale model, however, reveals that the reaction site is highly shielded. Moreover, in VI most R_1 and X and R_2 and Y pairs would be at bonding distances, yet no bonding is possible; the repulsive forces in such a species should necessarily be high.[42] Therefore, there are both experimental and theoretical reasons that make inversion mechanisms at an alkene carbon highly improbable.

If the preceding arguments against inversion processes are valid, then it follows that the low reactivity of vinyl halides as compared with alkyl halides can be rationalized adequately by electronic factors, for example, the increased electronegativity of the carbon and the partial double bond character of the carbon–halogen bond; steric factors would be far less important.[43]

Acknowledgment.—Exploratory work on this problem was first carried out by S. I. M. in the laboratory of R. M. Noyes at Columbia University

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(38) M. S. Newman, *J. Chem. Educ.*, **32**, 344 (1955).

(39) W. G. Dauben and K. S. Pitzer, ref. 2b, p. 57.

(40) G. S. Krishnamurthy and S. I. Miller, unpublished results.

(41) J. Weinstock and F. G. Bordwell have suggested that a process analogous to (5) involving a sterically stable vinyl carbanion could account for our observations. Since this would require that iodide be a powerful nucleophile and that the resulting carbanion should not react with the hydroxylic medium this mechanism was considered to be improbable.

(42) F. H. Westheimer, ref. 2b, p. 542.

(43) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5034 (1951).

and at the University of Michigan. A stimulating discussion with Dr. Noyes on the kinetic and mechanistic aspects of (8) is gratefully acknowledged. The financial assistance of the Research Corporation is sincerely appreciated.

CHICAGO 16, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Correlation of Solvolysis Rates. IV.[1] Solvent Effects on Enthalpy and Entropy of Activation for Solvolysis of *t*-Butyl Chloride[2]

BY S. WINSTEIN AND ARNOLD H. FAINBERG

RECEIVED MAY 13, 1957

In probing the basis of the success and limitations of linear free energy correlations of rates of solvolysis, the behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for solvolysis of *t*-butyl chloride toward solvent variation has been explored. The variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with solvent has been scrutinized in the large variety of solvents reported on previously. In five of six pure solvents, $\Delta S^{\ddagger}$ for solvolysis of *t*-butyl chloride is relatively constant at *ca.* −3 e.u. On the other hand, water is uniquely set apart from the other solvents, $\Delta S^{\ddagger}$ now being 15 e.u. higher. A similarly anomalous position is occupied by the solvent water in solvolysis of other materials. With the aid of Henry's law constants for *t*-butyl chloride, the $\Delta\Delta F^{\ddagger}$ due to a solvent change can be dissected into separate effects on the ground state and transition state, namely, $\Delta\Delta F^{0}{}_{v}$ and $\Delta\Delta F^{\ddagger}{}_{s}$, respectively. Henry's law constants at several temperatures make possible the analogous dissection of the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ terms. For changes of medium from one pure solvent to another in the case of *t*-butyl chloride solvolysis, $\Delta\Delta F^{\ddagger}{}_{s}$ tends to be of major importance. However, for the MeOH → HOH or EtOH → HOH solvent changes, $\Delta\Delta F^{0}{}_{v}$, related to the ground state, is of major importance. For solvolysis of *t*-butyl chloride in binary solvent mixtures, the behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ toward solvent composition tends to be complex. In this respect, the EtOH–HOH system is the most complex. For the various binary solvent systems, a linear relation between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ is the exception rather than the rule. An **ABC** classification system can be set up for characterizing the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior in solvolysis, and the symbolic terminology has been employed in summarizing and comparing the behavior of *t*-butyl chloride and a number of other substrates. As anticipated, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior in *t*-butyl chloride solvolysis in binary solvent mixtures is poorly accounted for by a simple electrostatic treatment. Examination of Henry's law constants for *t*-butyl chloride in MeOH–HOH mixtures show that both ground state and transition state contributions to the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values are important. Comparing the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior for *t*-butyl chloride with that for other substrates, it is evident that the various substances do not obey generalizations based solely on the nature of the solvent systems. Instead, as can be anticipated, the $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ behavior depends on substrate structure as well as on the nature of the solvent system. The pattern of behavior of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for solvolysis of a substrate molecule determines the effect of temperature variation on the precision of the $m\mathbf{Y}$ correlation of the rates of solvolysis of that substrate molecule. This matter is treated analytically.

The thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, for the solvolysis of the key substance, *t*-butyl chloride,[3] are of interest in probing the basis of the success and limitations of the linear free energy relationships[3] 1, 2 and 3. In relationship 1, $(k/k_0)_{\mathrm{RX}}$ is the ratio of first-order solvolysis rate constants of RX in a solvent and in a standard solvent, respectively, while $(k/k_0)_{\mathrm{RY}}$ is the analogous ratio for the substance RY. Relationship 3 makes use of a set of **Y** values for solvents equal to log (k/k_0) at 25° for the standard substance, *t*-butyl chloride. Thus, the **Y** values, or measures of solvent ionizing power, are based on a blend of specific and general solvent influences[3,4] appropriate to *t*-butyl chloride solvolysis.

$$\log\left(\frac{k}{k_0}\right)_{\mathrm{RX}} = m \log\left(\frac{k}{k_0}\right)_{\mathrm{RY}} \qquad (1)$$

$$\Delta\Delta F^{\ddagger}{}_{\mathrm{RX}} = m\, \Delta\Delta F^{\ddagger}{}_{\mathrm{RY}} \qquad (2)$$

$$\log\left(\frac{k}{k_0}\right) = \frac{-1}{2.303RT}\left(\frac{\partial \Delta F^{\ddagger}}{\partial \mathbf{Y}}\right)\mathbf{Y} = m\mathbf{Y} \qquad (3)$$

A further interest in the thermodynamic quantities of activation of solvolysis is based on their possible utility in diagnosis of mechanism.[5] However, before any safe generalizations can be drawn regarding the connection between mechanism and $\Delta S^{\ddagger}$, for example, the dependence of $\Delta S^{\ddagger}$ on solvent composition for known mechanisms needs to be explored.

The variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with solvent for the solvolysis of *t*-butyl chloride has been scrutinized in the large variety of solvents reported on in a previous paper.[3c] These results are reported and discussed in the present article.

Results

In Table I are summarized the first-order rate constants at 0° or 50° for solvolysis of *t*-butyl chloride in the various pure and mixed solvents. Most of the rate constants are new, a few representing duplication as indicated in the footnotes. In virtually all cases, the solvent mixtures were from the same batches as those employed to obtain the rates at 25.0° reported previously.[3c]

Also listed in the table are the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ calculated from the present and previous[3c] data. Based on the estimated probable error of the rate constants,[3c] $\Delta H^{\ddagger}$ is considered accurate to ±0.15 kcal./mole, and $\Delta S^{\ddagger}$ to ±0.5 e.u.

Some further comment on the present $\Delta H^{\ddagger}$ values is in order because reactions involving increase of charge, and therefore increased solvation, during passage into the transition state, commonly dis-

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Minneapolis, Minn., Sept. 16, 1955; page 52R of Abstracts.

(2) Research sponsored by the Office of Ordnance Research, U. S. Army.

(3) (a) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(4) E. Gelles, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954).

(5) *E.g.*, S. Winstein and R. Heck, THIS JOURNAL, **78**, 4801 (1956).