Vinylic Cations from Solvolysis. 30.[1] Bromide Exchange as a Reactivity–Selectivity Probe in Vinylic Solvolysis

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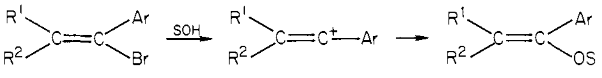
Abstract: Simultaneous exchange with radioactive Br^- and solvolysis of 9-(α-bromo-*p*-methoxybenzylidene)anthrone (**3a**), its p-methyl analogue (**3b**), and three α-anisyl-β,β-diarylvinyl bromides (**5a**, **5b**, and **5c**) in AcOH/NaOAc/Et_4NBr were studied. The reactions proceed via free vinyl cations and the dependence of k_t on the NaOAc concentration for **3a** and **5a** indicates the rare S_N2 (C^+) mechanism. The selectivity constants of the derived cations toward bromide and acetate ions $\alpha = k_{Br}/k_{OAc}$ increase with the reactivity of RBr, both in the family of the α-aryl-substituted (**3**) and in the family of the β-aryl-substituted (**5**) derivatives. Consequently, the reactivity–selectivity relationship rather than Ritchie's constant selectivity relationship applies for solvolytically generated free triarylvinyl cations. The exchange–solvolysis method is compared with the method based on common ion rate depression as reactivity–selectivity probes for the vinyl cations formed in the solvolysis. The exchange–solvolysis method is more accurate and measures the selectivity and the reactivity in independent processes. Caution should be exercised when comparing k_1 and α values which are measured by the two different methods, due to unkown salt effects on the two parameters.

In previous papers of this series[1–4] it was shown that the solvolysis of many α-arylvinyl halides (**1**) is accompanied by common ion rate depression by the liberated halide ion. This is taken as evidence that the product-forming intermediate is the free sp-hybridized α-arylvinyl cation (**2**) (eq 1). Application of a simple



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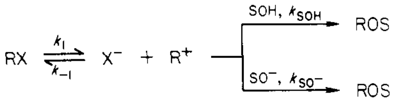
solvolysis scheme (eq 2) which involves capture of the free cation



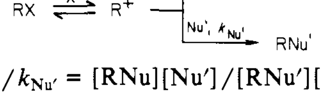
(2)

by the solvent SOH or its conjugate base SO^- gives eq 3 and 4

$$1/k_t = 1/k_1 + (\alpha'/k_1)f'(x) \tag{3}$$

$$1/k_t = 1/k_1 + (\alpha/k_1)f(x) \tag{4}$$

which show the decrease of the integrated rate constant k_t with the progress of the reaction. In these equations $f'(x) = (a - x)/\ln(a/(a - x))$ and $f(x) = [1/(1 - n)]n \ln(na/(na - x))/(\ln(a/(a - x)) - 1)$ are functions of the concentrations of the various species ($a = [RX]_0$, $x = [ROS]_t$, $n = [SO^-]_0/[RX]_0$). The k_1 value represents the solvolytic reactivity of RX which is presumably inversely proportional to the reactivity of R^+ and $\alpha' = k_{X^-}/k_{SOH}$ and $\alpha = k_{X^-}/k_{SO^-}$ are selectivity constants for competition of the pairs of nucleophiles X^- and SOH or X^- and SO^- toward R^+. The selectivity constants have been calculated by four different methods: (a) from the common ion rate depression by applying equations similar to eq 3 and 4;[5] (b) from the ratio of products obtained in a competitive reaction with two nucleophiles Nu and Nu′ (eq 5) (the selectivity constants are calculated by eq 6 with



(5)

$$k_{Nu}/k_{Nu'} = [RNu][Nu']/[RNu'][Nu] \tag{6}$$

the assumption that the rates of capture are of the same kinetic order);[6,7] (c) from an independent determination of the rates of product formation and the simultaneous incorporation of isotopically labeled X^- into the unreacted RX during the solvolyis giving selectivity constants which resemble α and α';[8] and (d) by using the ratios of directly measured rates of reaction of relatively stable carbonium ions with nucleophiles.[9]

Surprisingly, the relationship found between the stability of the ions and their selectivities is not the same when the different methods are used. The selectivities calculated by methods a–c for solvolytically generated ions are all higher for the RX which solvolyzes faster.[5–8] Since a higher solvolysis rate is usually associated with the formation of a more stable, i.e., less reactive,

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cation, these results indicate a reactivity–selectivity relationship for the cationoid intermediate. Linear reactivity–selectivity plots of log k (RX) vs. log $(k_{Nu}/k_{Nu'})$ were found for competition between the nucleophile pairs azide ion and water[6] or water and ethanol.[7a,b]

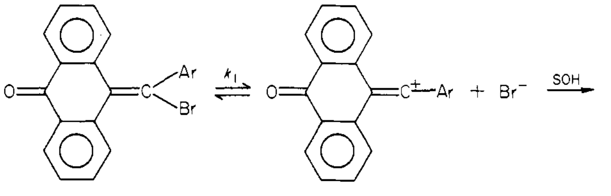
In contrast, the selectivity ratios obtained from the reaction of stable cations with nucleophiles (method d) were constant, in spite of large variations in the structure of R^+ and in the cation–nucleophile recombination rates.[9] This "constant selectivity rule" is formalized in eq 7, where N_+ is a nucleophilicity parameter.

$$\log (k_{Nu}/k_{H_2O}) = N_+ \qquad (7)$$

meter.[9] Equation 7 holds also for reactions at aromatic,[10a] vinylic,[10b] carbonyl,[10c] and sulfonyl carbon.[10d] Several explanations have been offered for the apparent contradiction of the mutual coexistence of the reactivity–selectivity and the constant selectivity rules. An attempt has been made to represent the constant selectivity as a special case of the reactivity–selectivity relationship.[11] It was also suggested that the two rules operate at different ranges of cation stability.[12] Ritchie suggested that the selectivity measured in solvolysis is an average selectivity for ion pairs and free ions and is not necessarily comparable to the selectivity of the free ion measured by him.[13]

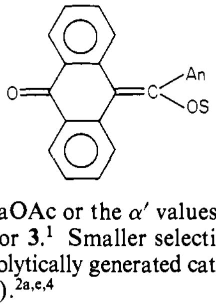
This suggestion can be evaluated if the selectivities of *solvolytically generated free ions* can be determined. This can be done by method a since common ion rate depression results from a competitive capture of a *free* cation by the two nucleophiles.[14] In contrast, incorporation of labeled X^- takes place at the free ion stage but may also involve exchange at the ion pair stage, whereas the selectivities determined by method b can arise from capture of any cationoid species.

Since the vinylic solvolysis of many systems **1** shows common ion rate depression and all or most of the products are derived from the free cations **2**, we applied this reaction for the determination of the selectivities of solvolytically generated free ions. It was found previously that the selectivities of cations **2** increase with the increased bulk of the β-substituted R^2 and R^1.[3c,4,15] In order to compare sterically similar ions, we solvolyzed compounds **3** (eq 8) and found that for the ions **4** the α values for the nucleophiles AcO⁻ and Br⁻ in AcOH/NaOAc or the α′ values for the Br⁻, TFE pair increased with k_1 for **3**.[1] Smaller selectivity differences were found between the solvolytically generated cations **6** differing in the β-aryl groups (eq 9).[2a,c,4]



3a, Ar = An
3b, Ar = Tol
3c, Ar = *o*-An

4a, Ar = An
4b, Ar = Tol
4c, Ar = *o*-An



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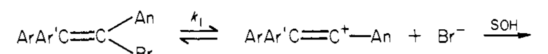
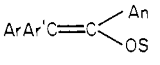


$$\mathrm{ArAr'C{=}C(An)Br} \underset{}{\overset{k_1}{\rightleftharpoons}} \mathrm{ArAr'C{=}C^{+}{-}An} + \mathrm{Br^-} \xrightarrow{\mathrm{SOH}}$$

5a, Ar = Ar′ = An
5b, Ar = An, Ar′ = Ph
5c, Ar = Ar′ = Ph

6a, Ar = Ar′ = An
6b, Ar = An, Ar′ = Ph
6c, Ar = Ar′ = Ph



$$\mathrm{ArAr'C{=}C(An)OS} \qquad (9)$$

Although these studies established that eq 7 is not applicable for solvolysis via ions **4** and **6**, method a has a severe drawback. Since k_t decreases during a run due to common ion rate depression, k_1 is obtained by extrapolation from the intercepts of eq 3 and 4. The slopes of the same equations give α and α′. Consequently, the selectivity and the reactivity are obtained from the same equation and the errors are interdependent. If the rate decrease within a run is strong, the extrapolation leads to severe errors in both $1/k_1$ and α or α′. The error in k_1 is not very important if the rate differences are large as between **3a** and **3b**, but it is important when the differences are small as between **5a** and **5b**. The errors in α for both **3** and **5** are important since the selectivity differences are usually much smaller than the reactivity differences.

Consequently, the observed reactivity–selectivity behavior should be substantiated by another selectivity measurement. Since compounds **3** and **5** give products from the free ions **4** and **6**, the selectivity constants were now measured for them in AcOH/NaOAc by following simultaneously the rates of vinyl acetate formation (k_t) and of incorporation of labeled bromide (k_{ex}) into unreacted RBr (method c). Rate decrease is not expected since an excess of Br⁻ is used, and the method is more accurate than method a since extrapolations are not necessary. Moreover, of all the methods used, it mostly resembles Ritchie's method (d) since the reaction rates for the two nucleophiles are determined independently.

Results

The solvolysis and exchange of 9-(α-bromo-*p*-methoxybenzylidene)anthrone **3a** and its *p*-tolyl analogue (**3b**) and of trianisylvinyl bromide (**5a**), *cis*-1,2-dianisyl-2-phenylvinyl bromide (**5b**), and 2,2-diphenyl-1-anisylvinyl bromide (**5c**) were conducted in AcOH, mostly buffered with 0.087 M NaOAc. These are conditions similar to those used previously for the determination of the α values by common ion rate depression. The reactions were conducted in the presence of relatively high concentration (0.071 M) of $Et_4N^{82}Br$ (Et_4NBr^*) in order to direct most of the reaction to the exchange route.

Product Formation. Under the above conditions the products from **3a** and **3b** were the ^{82}Br-labeled compounds **3a*** and **3b*** and 9,10-anthraquinone (**7**). The NMR of the solvolysis mixture of **3a** before the workup, even in the presence of a large concentration of NaOAc, showed only the presence of **7**. This was verified by TLC on a silica plate and by isolation of **7** from chromatography on a silica column.

Since the solvolysis of **3a** in the absence of Et_4NBr gives first the unrearranged acetate **8a** which then rearranges to 9-acetoxy-10-anisoylanthracene (**9a**),[16] both compounds may be the precursors of **7**. That the sequence of eq 10 is followed, at least partially, is shown by the study of the reaction by high-pressure LC. Peaks for **8a**, **9a**, and **7** are observed at low conversion. The peak for **8a** decreases with time with a simultaneous increase in the peak for **9a**. The peak for **9a** decreases at longer reaction time with a simultaneous increase in the peak of **7**. The concentrations of both **8a** and **9a** remain relatively low during the reaction. The decomposition of **9a** to **7** is catalyzed by Et_4NBr: reflux of **9a** in AcOH/NaOAc gave only traces of **7** after 12 days, but when Et_4NBr was added to a similar mixture, >50% of **7** was formed after 3 days. The mechanism of this reaction is not clear, and the fate of the anisyl-containing residue from **9a** is unknown.[17]

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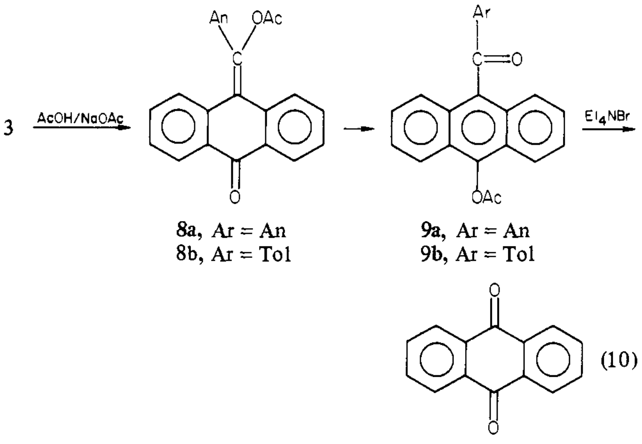
(17) 9,10-Anthraquinone is obtained by other reactions of **3a** which may involve the cation **4**. For example, it is an important product of the reaction of **3a** with silver trifluoromethanesulfonate in acetonitrile.



8a, Ar = An
8b, Ar = Tol

9a, Ar = An
9b, Ar = Tol

(10)

7

Since the effect of Et$_4$NBr on the **8a** → **7a** process was not studied, the contribution of this reaction to the formation of **7** is unknown.

A similar behavior was also observed in the reaction of **3b**. The product is again **7**, but **8b** and **9b** were never observed. This is probably due to the much lower solvolytic reactivity of **3b**.

The solvolysis of compounds **5** gives the triarylvinyl acetates **10** both in the absence and in the presence of Et$_4$NBr (eq 11).

$$\mathbf{5} \xrightarrow{\text{AcOH/NaOAc}} \underset{\mathbf{10}}{\text{Ar(Ar}'\text{)C=C(OAc)An}} \qquad (11)$$

For product formation according to eq 10 and 11 pseudo-first-order rate constants k_t were calculated for each run according to eq 12 since $[\text{NaOAc}]_t \approx [\text{NaOAc}]_0$. The k_t values for compounds **3** were obtained by following the disappearance of RBr by high-pressure LC. The values for compounds **5** were obtained from a follow-up of the formation of the vinyl acetates **10** by NMR or by high-pressure LC. A first-order plot for RBr is shown in Figure 1. By changing the concentration of the NaOAc, we observed a first-order dependency on [NaOAc] for **5a** (Table I) and for **3a** (Table II). The reaction is therefore described by eq 13, and the second order rate constants k_2 (eq 14) which are given in Table I for **5a** are nearly constant, except for a small salt effect.

$$-\ln ([\text{RBr}]_t/[\text{RBr}]_0) = k_t t \qquad (12)$$

$$\text{RBr} + \text{NaOAc} \xrightarrow{k_2} \text{ROAc} + \text{NaBr} \qquad (13)$$

$$k_2 = k_t/[\text{NaOAc}] \qquad (14)$$

Exchange. Uncorrected pseudo-first-order rate constants for the exchange reaction k_{ex} (eq 15) were determined from eq 16[18]

$$\text{RBr} + \text{Et}_4\text{N}^{82}\text{Br} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{R}^{82}\text{Br} + \text{Et}_4\text{NBr} \qquad (15)$$

$$\ln (n_\infty/(n_\infty - n_t)) = k_f([\text{RBr}]_0 + [\text{Et}_4\text{NBr}]_0)t = k_{ex}t \qquad (16)$$

which is valid only when $k_f = k_r$,[19] i.e., when the kinetic isotope effects on the forward and the backward exchange reactions are equal. This assumption is reasonable since the isotope effects are negligible for the ^{79,81}Br/^{82}Br exchange reaction. In eq 16 n_t is the specific activity of the labeled RBr at time t, and n_∞ is its specific activity at equilibrium. Since vinyl acetates are formed during the exchange, the equilibrium value n_∞ cannot be obtained from the graphs of the activity incorporated in the vinyl bromides. Hence, the theoretical n_∞ values (eq 17) in which n_{total} is the specific activity of the total solution were used. Model calculations show that a variation of 1% in n_∞ gives a variation of 1.5% in k_{ex}.

$$n_\infty = n_{\text{total}}([\text{RBr}]_0/([\text{RBr}]_0 + [\text{Et}_4\text{NBr}]_0)) \qquad (17)$$

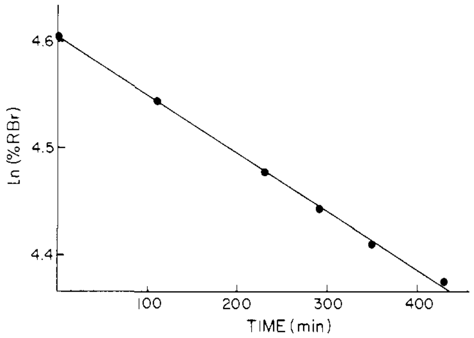


Figure 1. First-order plot for the acetolysis of 4.7 × 10^{-3} M **5a** in AcOH/8.7 × 10^{-2} M [NaOAc]/7.1 × 10^{-2} M [Et$_4$NBr] at 120 °C.

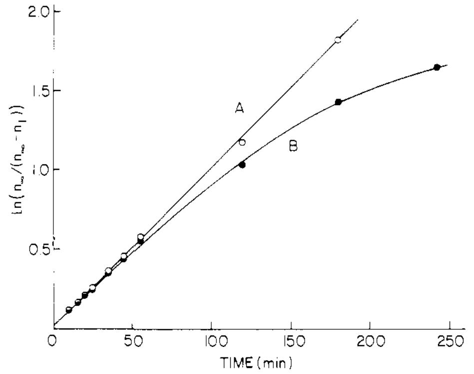


Figure 2. First-order plot for the exchange of 4.7 × 10^{-3} M **5a** in AcOH/8.7 × 10^{-2} M [NaOAc]/7.1 × 10^{-2} M [Et$_4$NBr*] in AcOH at 120 °C: (A, ○), corrected for the concurrent solvolysis; (*B*, ●), uncorrected for the concurrent solvolysis.

Table I. Effect of NaOAc on the Solvolysis of 5a in AcOH/Et$_4$NBr/NaOAc at 120 °C[a]

10^3[NaOAc], M	$10^7 k_t$, s^{-1}	$10^4 k_2$, M^{-1} s^{-1}	$10^4 k_1$, s^{-1} [b]
87	89 ± 1	1.02 ± 0.01	1.69 ± 0.02
96	98 ± 1	1.02 ± 0.01	1.69 ± 0.02
174	187 ± 1	1.07 ± 0.005	1.87 ± 0.02

[a] [5a] = 4.7 × 10^{-3} M; [Et$_4$NBr] = 7.1 × 10^{-2} M. The decrease of 5a was followed by high-pressure LC. [b] Calculated from eq 21.

Table II. Effect of Concentration Changes on $k_{ex}{}^{cor}$ and k_t for 3a in AcOH at 120 °C

10^3[3a], M	10^3[NaOAc], M	10^3[Et$_4$NBr], M	$10^5 k_{ex}{}^{cor}$, s^{-1}	$10^7 k_t$, s^{-1}	α	$10^5 k_1$, s^{-1}
6.5		71	59 ± 1			54 ± 1[a]
6.5	87	71	64 ± 1	96 ± 1	74.8	60 ± 1
6.5	174	71	68 ± 1	206 ± 5	74.1	64 ± 1
6.5	87	142	79 ± 1	62 ± 1	74.6	76 ± 1
40.0	87	71	94 ± 1	102 ± 2	72.2	61 ± 1

[a] Calculated from a combination of eq 20 and 21.

The k_{ex} values of eq 16 have to be corrected both for product formation and for the natural decay of ^{82}Br which has a half-life of $t_{1/2}$ = 35.9 h. Analysis of the simultaneous solvolysis and exchange gives the corrected k_{ex} values ($k_{ex}{}^{cor}$) of eq 18, where

$$k_{ex}{}^{cor}t = \ln (n_\infty/(n_\infty - n_t)) - \ln [e^{k_t t} - (e^{k_t t} - 1)(n_\infty/(n_\infty - n_t))] \qquad (18)$$

the second term on the right represents the correction due to product formation. Correction for the decay was introduced by using the expression $n_t{}^{cor} = n_t e^{+\lambda t}$ where $\lambda = 0.69/t_{1/2}$. The first-order behavior of the exchange process when correction for product formation is taken into account (eq 18) is compared with the deviation from first-order behavior when such correction is

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Table III. Kinetic Data for the Solvolysis and Exchange in AcOH/NaOAc/Et_4NBr^* at 120 °C[a]

RBr	10^3[RBr], M	$10^7 k_t$, s^{-1}	$10^5 k_{ex}^{cor}$, s^{-1}	α[d]	$10^5 k_1$, s^{-1} [e]
3a	6.5	96 ± 1[b]	64 ± 1	75 ± 1.4	59.7 ± 1.8
	4.7	92 ± 1[b]	60 ± 1	75 ± 1.4	57.2 ± 1.8
3b	6.5	0.77 ± 0.05[b]	0.084 ± 0.002	12.2 ± 0.8	0.084 ± 0.011
5a	6.5	114 ± 1[c]	22 ± 1	21.7 ± 0.7	21.3 ± 0.9
	4.7	89 ± 1	17 ± 0.5	22.0 ± 1.0	16.9 ± 0.9
5b	6.5	75 ± 2[c]	13 ± 1	19.5 ± 1.6	12.7 ± 1.4
	4.7	58 ± 2	9.7 ± 0.3	19.2 ± 0.9	9.7 ± 0.6
5c	6.5	53 ± 2[c]	8.8 ± 0.2	18.6 ± 0.8	8.6 ± 0.5

[a] [NaOAc] = 8.7×10^{-2} M; [Et_4NBr^*] = 7.1×10^{-2} M. Reaction followed by the decrease of RBr by high-pressure LC. [b] The main product is 9,10-anthraquinone. [c] The increase of [ROAc] was followed by NMR. [d] Calculated by eq 20. [e] Calculated by eq 21.

not introduced (eq 16) in Figure 2.

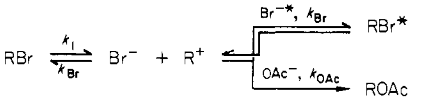
The effect of the change in the concentrations of RBr, NaOAc, and Et_4NBr on the k_{ex}^{cor} values is given in Table II. The values increase with the increase in the concentration of each of these species. The parameter b of the "normal" salt effect[20] was calcualted for the ionization process by using the k_1 values (cf. eq 19) of Table I for **5a** and of Table II for **3a**. For the solvolysis of **5a**, b(NaOAc) = 1.4 ± 0.3, and for the solvolysis of **3a**, b(NaOAc) = 1.1 ± 0.2 and $b(Et_4NBr)$ = 5.1.

The solvolysis and the exchange reactions were conducted in duplicate or triplicate and the average rate constants and their errors together with the derived selectivity constants α and k_1 values of eq 2 (see below) are summarized in Table III.

Discussion

The Capturing Nucleophile in AcOH/NaOAc. The identity of the nucleophile capturing R^+ in solvolytic S_N1 reactions via free cations usually cannot be determined by kinetics since the capture takes place after the rate-determining step. It can be determined from the nature of the nucleophile-incorporated product but not when two nucleophiles such as the solvent SOH and its conjugate base SO^- form the same product (eq 2). The problem is important in vinylic solvolysis in AcOH buffered by NaOAc, and in previous work[1,3,4] four types of arguments suggested that the nucleophile capturing R^+ is the acetate ion: (a) the decrease in the extent of the degenerate rearrangement of the "hot" trianisylvinyl cation **6** by added NaOAc,[1,21] (b) the lower extent of isomerization of **5b** to its trans isomer (via **6b**) on addition of NaOAc,[3a] (c) the better agreement with eq 3 than with eq 4,[1,3d] and (d) the dependence of the α and the α' values on [NaOAc].[1,3a,15] A straightforward kinetic evidence for this conclusion is achieved now for **3a** and **5a**. Whereas most S_N1 reactions are first order since $k_{SOH}[SOH] \gg k_{-1}[X^-]$ (cf. eq 2), we observe now the less common situation when $k_{-1}[X^-] \gg k_{SOH}[SOH]$, $k_{SO^-}[SO^-]$ in the presence of Et_4NBr. The cation–nucleophile reaction becomes rate determining under solvolytic conditions; i.e., the S_N1 process becomes the rarely observed S_N2 (C^+) process.[22] The first-order dependence on [NaOAc] under these conditions (Tables I and II) indicates that OAc^- is the nucleophile capturing **4a** and **6a**. Since OAc^- is a better nucleophile than AcOH, the same conclusion holds for cations of higher or similar selectivities such as **6b** and **6c**, regardless of whether they obey the reactivity–selectivity relationship or eq 7. However, it is not clear if this conclusion is also applicable for the capture of **4b**.

The Reactivity–Selectivity Relationship. Modification of eq 2 and application of designations used previously for the rate coefficients[1,3a] gives eq 19 which accounts for both the solvolysis



(19)

and the exchange. The selectivity constant α for competition between Br^- and OAc^- is given in terms of the observed rate constants for solvolysis and exchange by eq 20. Table III gives

$$\alpha = k_{Br}/k_{OAc} = k_f/k_2 = k_{ex}^{cor}[NaOAc]/k_t([RBr]_0 + [Et_4NBr]_0) \quad (20)$$

the α values for our compounds. Although both k_t and k_{ex} are lower at low [RBr], the α values remain constant when [RBr] changes 1.4-fold (Table III) and they change only little when [RBr] changes 6.1-fold (Table II).

Since the real reactivity measures of the ions, i.e., k_{Br} and k_{OAc}, cannot be obtained, the ionization rate constants of RBr (k_1) are taken as a measure of the stabilities and the inverted reactivities of the ions.[23] In the case of common ion rate depression the k_1 values were frequently obtained by a steep and inaccurate extrapolation.[3,15] An advantage of the present method is that extrapolation is not required. A stead-state treatment of eq 19 enables the calculation of k_1 values by eq 21, and they are given in Tables I–III.

$$k_1 = k_t(1 + \alpha[Et_4NBr]/[NaOAc]) \quad (21)$$

According to eq 19 the free ion formed in the presence of NaOAc and Et_4NBr^* gives either ROAc or the labeled and nonlabeled RBr. Consequently, in the absence of ion pair return with exchange the ionization rate constant should be equal to the sum of the rate constants for solvolysis and exchange (eq 22). Table III shows that this is indeed the case within the combined experimental errors.

$$k_1 = k_t + k_{ex}^{cor} \quad (22)$$

Table III and eq 22, in turn, corroborate the reaction scheme of eq 19 which does not involve a kinetically significant ion pair in the solvolyis and the exchange processes. The k_t/k_1 values of 0.016–0.09 indicate that ≥91%, ≥94%, and ≥98% of the products from **4b**, **6**, and **4a**, respectively, are formed from the free cation.[14] A significant exchange with Br^{-*} at the ion pair stage will increase k_{ex}^{cor} without affecting k_t and in this case k_{ex}^{cor} will be higher than k_1.[24] Small differences in this direction were found (Table III), but they are usually within the combined experimental error and cannot account for more than 5% exchange via the ion pairs. Ion pairs are involved in the return during the acetolysis of **5b** and probably of other compounds **5**, but their observed reactions are intramolecular and they are unreactive toward an external nucleophile.[3a]

The fact that the α values for the five ions differ from one another shows clearly that the selectivity toward Br^- and AcO^- in AcOH is not independent of the cation, as required by eq 7. Although the para substituents in the aryl groups have no steric influence on either the reactivity or the selectivity, the steric crowding around the reaction center or the vacant orbital is higher for species **3** and **4** than for **5** and **6**. Consequently, the comparisons are justified only within each family of compounds.[1,4]

The selectivities of R^+ and the reactivities of RBr increase in parallel in both series. For the α-substituted systems **3** the dif-

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[24] The assumption that the ion pair R^+X^- does not exchange its X^- with external X^- served as a partial basis in the evaluation of the extent of ion pair return during the solvolysis of **5a**.[3a,b]

Table IV. Kinetic Parameters obtained from Common Ion Rate Depression in AcOH/NaOAc at 120.3 °C[a]

RBr	$10^5 k_1$, s^{-1}	α	ref
3a	12	32	1
5a	5.9	17.7	15
5b	4.1	21.3	3a
5c	1.9	15.3	15

[a] [RBr] = 0.035-0.044 M; [NaOAc] = 0.084-0.088 M.

ferences are appreciable: $\alpha(\mathbf{4a})/\alpha(\mathbf{4b}) = 6$ and $k_1(\mathbf{3a})/k_1(\mathbf{3b})$ $(\mathbf{3a})/k_1(\mathbf{3b}) = 711$; i.e., Brown's ρ^+ value[25] is -6.1 and $\Delta \log k_1/\Delta \log \alpha$ value is 3.66. The differences for the α-substituted systems **5** are much smaller: $\alpha(\mathbf{5a})/\alpha(\mathbf{5c}) = 1.17$ and $k_1(\mathbf{5a})/k_1(\mathbf{5c}) = 2.5$; i.e., Hammett's ρ value assuming an additivity effect of the two rings is -0.73, and $\Delta \log k_1/\Delta \log \alpha = 5.75$.

The values for both systems are similar to those found earlier by using the method of common ion rate depression and eq 4. For system **3**, $\rho^+ = -6.0$ and $\Delta \log k_1/\Delta \log \alpha = 4.4$ in 1:1 AcOH-Ac_2O,[1] whereas for system **5** $k_1(\mathbf{5a})/k_1(\mathbf{5c}) = 3.35$, $\alpha(\mathbf{5a})/\alpha(\mathbf{5c}) = 1.21$, and $\Delta \log k_1/\Delta \log \alpha = 6.3$ in AcOH.[2a] The importance of this result is that the error associated with the α values obtained by common ion rate depression is higher than that by the present method. The nearly quantitative agreement between the two methods enhances the confidence in the use of the many results obtained by the former method.[4]

The reactivity-selectivity relationship observed for system **3** was discussed previously[1] in connection with the suggestion of a curved reactivity-selectivity relationship for the reaction of carbonium ions with nucleophiles.[12] The results for system **5** substantiate this conclusion. In spite of the small selectivity differences and the associated relatively high errors, it is clear that a decreased selectivity follows an increased reactivity of R^+ (i.e., lower $k_1(RX)$). *Consequently, for α-arylvinyl cations eq 7 is not obeyed when either the α- or the β-aryl substituent is modified.* In contrast, increase in the bulk of both the α-[3d,26] or the β-aryl group[1,4] or in the rigidity of the ions (cf. ions **4** vs. ions **6**)[1] or increase in the electron-donating ability of the α- and the β-aryl groups increases the selectivities of the ions.

Comparison of the Solvolysis-Exchange and the Common Ion Rate Depression Methods as Selectivity Probes. The k_1 and the α values obtained now by the solvolysis-exchange method (Table III) are compared with the values obtained by common ion rate depression at nearly the same temperature (Table IV).[27] In contrast with expectation, the values are not the same. The k_1 and the α values of Table III are 3-5 times and 0.9-2.3 times, respectively, of the k_1 and α values of Table IV. A correction for the normal salt effect of Et_4NBr[20] by using a b value of 5.1 (cf. Table II) reduces the k_1 values in the exchange experiments and the gap between them and the values of Table IV by a factor of 1.36.

Another correction is required to account for the 1 order of magnitude lower concentrations of RBr used in the exchange experiments. From Tables II and III, k_{ex} for **3a** at 0.04 M RBr is higher by 47% than k_{ex} at 0.0065 M, whereas k_{ex} for **5a** and **5b** at 0.0047 M are 25% lower. In contrast, in the solvolysis of **5b** in the absence of Et_4NBr the k_1 value at 0.0044 M RBr was 1.26 times higher than at 0.044 M.[3a] This correction closes the gap between the k_1 values of the two methods for compounds **5**, while the small residual difference between the k_1 values for **3a** is probably due to the extrapolation required for obtaining k_1 by common ion rate depression.

The similarity of the corrected k_1 values obtained by the two methods indicates the validity of the assumption that the same process is being measured by both methods. However, although the corrections are supported experimentally, it is not clear why k_1 for **5a** and **5b** but not for **3a** shows a dependence on [RBr] and why the dependence is opposite in both methods. Moreover, although $b = 5.1$ for Et_4NBr in the presence of 0.071 M NaOAc and $b = 4.4$ for Bu_4NBr in the presence of 0.011 M NaOAc in the solvolysis of **5b**, it is not clear to what extent b for one salt depends on the concentration of the other salt. The overall salt effect should reflect the combined effect of the several ion pairs present in the low-dielectric AcOH.

The higher α values obtained by the solvolysis-exchange method could be due to two reasons. First, the larger difference between the α values of Tables III and IV is for **3a** for which the α value is the highest. The extrapolation error associated with the use of eq 4 is the largest in this case, suggesting that an appreciable part or most of the difference in the α values is due to this extrapolation. Second, the concentration terms $[OAc^-]$ and $[Br^-]$ used in both treatments were taken as equivalent to the stoichiometric salt concentration, although the main species in AcOH are the ion pairs Na^+OAc^-, Na^+Br^-, $Et_4N^+Br^-$, and $Et_4N^+OAc^-$. Dilution will increase the dissociation to the free Br^- and OAc^- ions, and since free ions are more reactive than ion pairs,[28] the rates of reactions with R^+ will increase. The fact that the α value measured by common ion rate depression increases on dilution[3a] suggests that the dissociation of the formed Na^+Br^- increases more than that of Na^+OAc^- on dilution. The α values in the solvolysis-exchange method were measured in the presence of relatively high concentration of Et_4NBr and similar or somewhat lower concentration of NaOAc than in the common ion rate depression method. The equilibrium constant for the ion pair exchange reaction (eq 23) is unknown except that it probably differs from

$$Et_4N^+Br^- + Na^+OAc^- \rightleftharpoons Et_4N^+OAc^- + Na^+Br^- \quad (23)$$

unity as found for the equilibrium of eq 24.[29] Consequently, the

$$Me_4N^+Cl^- + Na^+OAc^- \xrightleftharpoons{K = 0.33} Me_4N^+OAc^- + Na^+Cl^- \quad (24)$$

different α values of the two methods may reflect different extents of ion pair dissociations. However, the near constancy of the α values of Table II shows that this effect is small in the concentration range of the salts used in Table II.

Both methods share several advantages as selectivity measures over the method which uses the product analysis,[1] but the solvolysis-exchange method has two main advantages over the common ion rate depression method. First, the reactivity and the selectivity are measured independently, whereas in the latter method they are obtained from the same equation and they are not independent. Second, severe extrapolations which lead to large errors, especially at high selectivities, are included in the treatment of the common ion rate depression, even if the linear regression of eq 4 is used. Such extrapolations are not required in the solvolysis-exchange method which should therefore be regarded as a superior probe for the phenomenon of reactivity-selectivity for a family of compounds. However, in view of the above discussion caution should be exercised when comparing the reactivities k_1 or the selectivities α with the values obtained by other methods, especially at different salt concentrations. The presence of large concentrations of Et_4NBr affects these parameters and may also affect the nature of the product.[30a]

Experimental Section

NMR analysis was carried out with a JEOL JNM-PS-100 spectrometer. High-pressure LC analyses were performed with a Kipp constant-flow high-pressure LC system, and the detection wavelength was 254 nm. Radioactivity measurements of the γ-emission of ^{82}Br were

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(30) (a) The mechanism of the Et_4NBr-catalyzed transformation **9** → **7** is not clear although multistep routes involving an initial attack of Br^- or OAc^- on the carbonyl group of **9** may be written. (b) The byproducts of the reactions **3a,b** → → **7** must prefer the water over the hexane layer or/and be nonbromine containing. High-pressure LC gives no indications for their occurrence in the hexane solution after workup, and the radioactivity measurements show no deviations from the first-order kinetic behavior, expected when radioactive byproducts would be formed.

conducted with a Philips scintillation counter with a well type thallium-activated sodium iodide crystal. Only the photopeak at 0.77 MeV was counted.

Materials and Solvents. The preparation of **5a**, **5b**, and **5c**[31] and of the anthronylidene derivatives **3a** and **3b**[16] was described previously. The vinyl acetate **8** and its isomer **9** were available from a previous study.[16] 9,10-Anthraquinone, mp 286 °C, was obtained from Ciba. Et$_4$N^{82}Br was obtained from the Interuniversity Reactor Institute in Delft, The Netherlands. It was prepared by neutron irradiation of Et$_4$NBr. The n,γ reaction on the natural occurring mixture of Et$_4$N^{79}Br and Et$_4$N^{81}Br results in the formation of Et$_4$N^{80}Br (half-lives 4.5 h and 18 min) and Et$_4$N^{82}Br (half-life 35.9 h). After appropriate time the amount of Et$_4$N^{80}Br is negligible. Purification of AcOH was described previously.[31b]

Stability of 9-(α-Bromoanisylidene)anthrone (3a). A mixture of **3a** (2.54 g, 6.5 mM) and tetraethylammonium bromide (14.9 g, 71 mM) in AcOH (20 mL) was refluxed for 6 days. TLC analysis showed only traces of 9,10-anthraquinone.

Stability of 9-Acetoxy-10-anisoylanthracene (9a). (a) A mixture of **9a** (20 mg, 0.07 mM) and sodium acetate (100 mg, 1.22 mM) in AcOH (15 mL) was refluxed for 12 days. TLC on a silica plate showed only the unreacted **9a** up to 11 days, but traces of 9,10-anthraquinone were observed after 12 days.

(b) A mixture of **9a** (20 mg, 0.07 mM), sodium acetate (100 mg, 1.22 mM), and tetraethylammonium bromide (256 mg, 1.22 mM) in AcOH (15 ml) was refluxed for 3 days. TLC on a silica plate showed the formation of >50% 9,10-anthraquinone which was identical with an authentic sample.

Kinetic Procedure. A reaction mixture of 40–50 mL was used for the experiments. With all the compounds except for **3b** no problems were encountered. Erratic kinetic results with the slow reacting **3b** were traced to some evaporation of the solvent after long reaction times and good results were obtained for this compound by using the sealed ampules technique. Because of the slow rate of reaction of **3b**, the product formation for this compound was only followed up to 20% conversion and its exchange up to 40%.

The solvolysis reaction was analyzed by two methods. (a) Analysis by NMR: at regular intervals 5-mL samples were withdrawn from the solution and added to hexane (50 mL); the mixture was washed twice with saturated NaHCO$_3$ solution (50 mL), separated, and dried (MgSO$_4$); the solvent was evaporated, and the remaining solid was dissolved in CDCl$_3$ and analyzed by NMR. (b) Analysis by high-pressure LC: samples of 0.5 or 1.0 mL were withdrawn and added to hexane (10.0 mL) containing a known amount of anisole; after being washed and separated, 20 μL of the hexane solution was injected into an high-pressure LC column. For **3a** a 15-cm Partisil column with 10% THF in hexane as the mobil phase was used. At a flow rate of 1.5 mL/min the retention times were as follows: anisole (internal standard), 1.4 min; 7, 2.2 min; **9a**, 7 min; **8a**, 10.5 min. The retention times for the reaction of **3b** on a 25-cm silica column with 15% THF in hexane as the mobil phase at a flow rate of 2 mL/min were as follows: anisole, 1 min; **3b**, 3.2 min; **7**, 3.6 min. For **5a** and **5b** a 15-cm Partisil column with 10% THF in hexane as the mobil phase was used. The retention times were as follows: **5a**, 5.3 min; trianisylvinyl acetate, 9.6 min (at a flow rate of 1.5 mL/min); **5b**, 4.3 min; its corresponding *E*- and *Z*-acetates, 6.2 and 6.7 min (at a flow rate of 1.2 mL/min).

For the exchange reaction 0.5- or 1.0-mL samples were withdrawn at the appropriate times and added to hexane (10.0 mL). After careful washing with water to remove all the inorganic bromide, 5.0 mL of the solution were analyzed for radioactivity by counting the 0.77-MeV peak of the ^{82}Br-γ spectrum with a scintillation counter. In all cases (after correction for the formation of the products indicated) a first-order kinetic behavior of the exchange was observed.[30b]

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Reactions of Difluorosilylene with Halogen-Substituted Ethylenes. A Reinvestigation of the Reaction Mechanism

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Abstract: In supporting our recent discovery of the gas-phase reaction of monomeric difluorosilylene, reactions of SiF$_2$ with *trans*- and *cis*-difluoroethylene, vinyl chloride, and vinyl fluoride are studied in the gas phase. Compounds from insertion of monomeric SiF$_2$ into carbon–halogen bonds are the only type of product obtained in these reactions. In order to avoid the complication that might be brought into the case of cocondensation experiments by the gas phase reactions prior to condensation, we carried out well-controlled "alternate layer" experiments for some of the reactions. The results show definitely that some SiF$_2$ remains monomeric at −196 °C. When the results of the reactions under various experimental conditions are compared, the conclusion shows that the best explanation for the reaction mechanism is the one involving $\cdot(\mathrm{SiF}_2)_n\cdot$ diradicals with $n = 1,2,3, \cdots$ etc., in which the silirane intermediate can be considered as a special case of $n = 1$.

The reaction mechanism of difluorosilylene has long been controversial.[1,2] Although for a long time we have believed that $\cdot(\mathrm{SiF}_2)_n\cdot$ diradicals are mainly responsible for the observed chemistry of difluorosilylene in cocondensation experiments, other possibilities are never ruled out.[3-5] The synthesis and some chemistry of difluorosilirane reported recently by Seyferth suggested an alternative interpretation of the observed chemistry of difluorosilylene,[1] which was backed up by a ^{29}Si NMR study of the $[-\mathrm{CH(CH_3)CH_2SiF_2}-]_n$ polymer formed in the reaction of SiF$_2$ with propene.[6]

In a recent communication[7] we have demonstrated that under proper conditions monomeric SiF$_2$(g) can react in reasonably good yield with 1,3-butadiene in the gas phase. Because the center of the controversy lies on whether $\cdot(\mathrm{SiF}_2)_n\cdot$ diradicals are involved

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