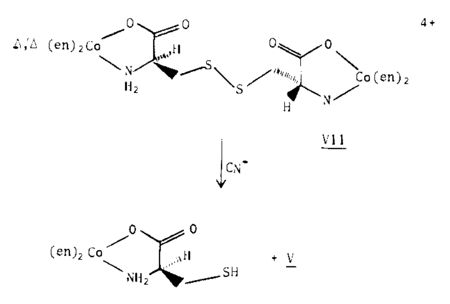
azoline ring has formed at a different site. The rearrangements are depicted in Scheme I which also outlines a plausible mechanism. Note that the five-membered ring formed at the amino acid N atom is preferred to a seven-membered ring involving the N atom of an adjacent ethylenediamine.

The known absolute configuration of (*R*)-cysteine, coupled with the known configurations of the reactant, fixes the chirality about cobalt as Δ which confirms the suspected retention of configuration at both centres during the reaction. The X-ray anomalous dispersion results are also consistent with this assignment (weighted *R* values for the Δ and Λ configurations 0.0960 and 0.0968, respectively). The thiaamidine moiety is delocalized over both N atoms since the C–N bond lengths are almost the same (1.32 (3) and 1.29 (2) Å) and the atoms Co, N(1), C(2), C(4), and N(6) are essentially coplanar (mean deviation 0.015 Å). This indicates that both N protons should be found on the N atom exo to the ring even though they were not located crystallographically unambiguously. Such an assignment is in keeping with other coordinated amidine structures where the protons have always been found on the uncoordinated N atom.[6-8] Furthermore, the ^{1}H NMR spectrum in MeSO-d_6 showed an isolated NH_2 resonance (δ 7.25, 2 protons) which indicates the N-proton distribution in the crystal is retained in solution. In D_2O or DCl, however, exchange was too rapid to allow the observation of the NH_2 signal. Isomer V was deprotonated by OH^- and the isolated perchlorate salt[9] gave an NH signal at δ 5.33 (1 H) in Me_2SO-d_6. Deprotonation of the exo NH_2 is implicated (VI).

Under the basic conditions of the CN^- addition (pH ~9), mutarotation of the configuration about cobalt in the reactant sulfenamide would be rapid ($t_{1/2} \sim 20$ s).[3] The results show however that the Δ configuration is retained and therefore nucleophilic attack at S must be exceedingly rapid under the conditions (0.1 M CN^-, $t_{1/2} \lesssim 1$ s, 20 °C). This conclusion is in keeping with previously reported reductions and additional observations on the sulfenamide II using BH_4^-, $S_2O_4^{2-}$, SO_3^{2-}, and RS^- ions.[2,3] All of the reagents react rapidly and cleave the sulfenamide bond without mutarotation about cobalt.

An alternative stereospecific synthesis of the 2-aminothiazoline-4-carboxylato chelate, V, was found through the action of CN^- on the cystine dimer, VII, Scheme II, of known

Scheme II



structure and absolute configuration.[2] Half of the dimer yields the thiazolinecarboxylato chelate; the other half yields the N,O-bound cysteinato complex, VIII. This result also confirms the absolute configuration derived from the sulfenamide and lends support to the mechanistic proposals in Scheme I. Both reactions should take place through the dangling thiocyanate intermediate III. Also it supports earlier observations[10] on the reaction between CN^- and uncoordinated (*R*,*R*)-cystine which was believed to give the aminothiazoline carboxylate reported here.

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Supplementary Material Available. Atomic parameters (Table 1), bond distances, angles, dihedral angles, and mean planes (Table 2), and listings of observed and calculated structure factors (Table 3) (5 pages). Ordering information is given on any current masthead page.

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(3) G. J. Gainsford, W. G. Jackson, A. M. Sargeson, and A. D. Watson, unpublished work.
(4) Anal. Calcd for $CoC_8H_{21}N_6SCl_2O_{10}$: C, 18.4; H, 4.1; N, 16.1; S, 6.1; Cl, 13.6.Found: C, 18.5; H, 4.2; N, 16.1; S, 6.0; Cl, 13.6.
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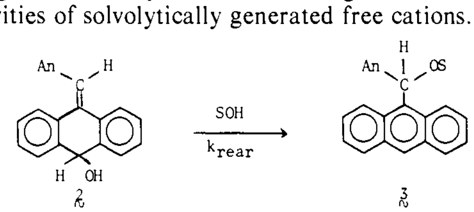
Vinylic Cations from Solvolysis. 28.[1] Solvent Dependency of the Solvolytic Site of 9-(α-Bromoanisylidene)-10-hydroxy-9,10-dihydroanthracene

Sir:

In a recent communication[1] we reported the preparation and the rates of solvolysis (k_t) and loss of optical activity (k_α) of an optically active vinylic compound, 9-(α-bromoanisylidene)-10-hydroxy-9,10-dihydroanthracene (**1**), in TFE. It was concluded that ion pairs are not involved in the solvolysis, indicating the suitability of **1** and its analogues for studying the selectivities of solvolytically generated free cations. A com-



peting initial solvolysis of the 10-hydroxy group was excluded, among other evidence, by the lower solvolytic rearrangement rate (k_{rear}) of the nonbromo analogue **2** to **3**. We now report that the initial solvolytic site of **1** is solvent dependent.

Table I gives k_t values (measured either by UV or titrimetrically) and k_α values for **1** and k_{rear} values for **2** in 80% EtOH and AcOH. In 80% EtOH $k_\alpha/k_t = 1.02 \pm 0.04$ and common ion rate depression[2] within a run was not detected, although k_t in the presence of Bu_4NBr (k_d) is reduced. Combination of

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Scheme I

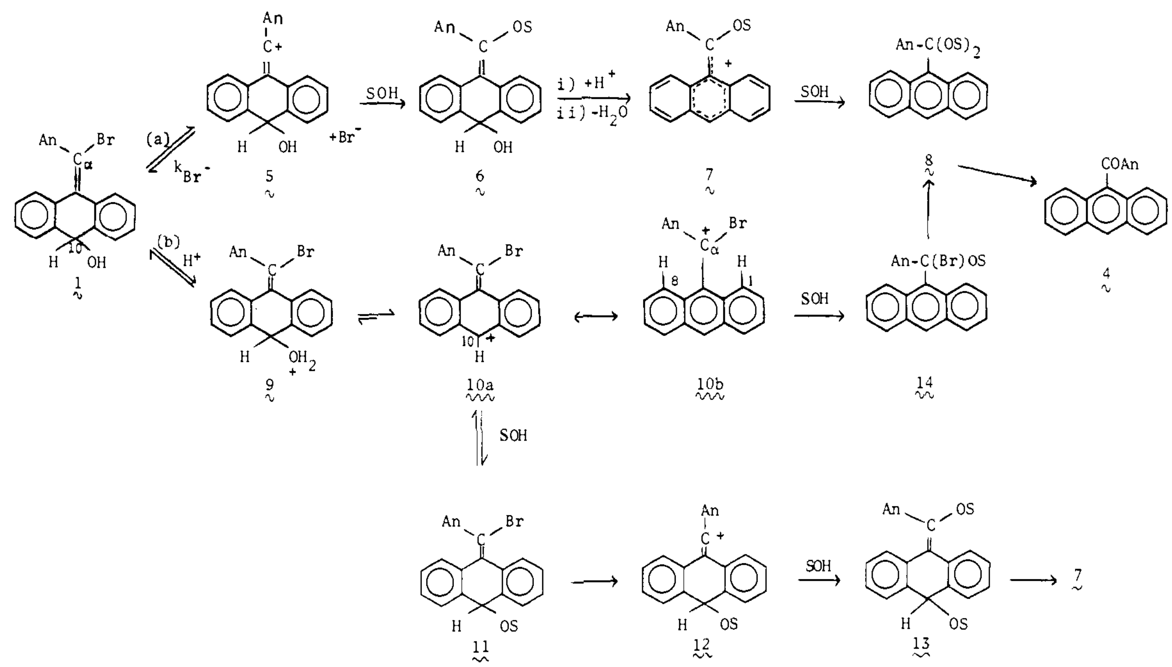


Table I. K_α, k_t, and k_{rear} Values in Several Solvents

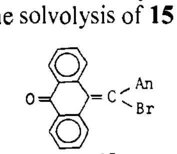
compd[a]	solvent	base[b]	Bu_4NBr, M	T, °C	k	$10^6\,k$, s^{-1}
1	80% EtOH	2,6-lutidine		100	k_α	127 ± 1.8
					$k_t{}^c$	106.4 ± 1.3
	80% EtOH	2,6-lutidine		100	$k_t{}^c$	114.7 ± 2.7
					$k_t{}^d$	125 ± 2.0
			0.01	100	$k_t{}^d$	79.9 ± 0.9
			0.1	100	$k_t{}^d$	43.5 ± 0.9
2	80% EtOH	2,6-lutidine		100	k_{rear}	113 ± 2
			0.01	100	k_{rear}	117 ± 8
1	AcOH	NaOAc		29	k_α	11.2 ± 0.06
	AcOH	NaOAc		49.6	k_α	105 ± 8.1
	AcOH	NaOAc		49.6	$k_t{}^c$	0.78 ± 0.02
	AcOH	NaOAc		49.6	$k_t{}^d$	0.77 ± 0.02
2	AcOH	NaOAc		20	k_{rear}	1115 ± 15
1	AcOH-Ac_2O^e	NaOAc		49.6	k_α	47.7 ± 1.0
	AcOH-Ac_2O^e	NaOAc	0.01	49.6	k_α	57.3 ± 2.8
	AcOH-Ac_2O^e	NaOAc		49.6	$k_t{}^c$	0.34 ± 0.01

[a] [Substrate], 0.002 M. [b] [Base], 0.004 M in 80% EtOH and AcOH and 0.008 M in 1:1 AcOH-Ac_2O. [c] By following the formation of **4** by UV. [d] By Br^- titration. [e] 1:1 v/v.

the equations for common ion rate depression[2] and normal salt effect[3] gives a relationship from which a normal salt effect parameter, $b = 19$, and a selectivity constant, $\alpha = k_{Br^-}/k_{80\%\ EtOH} = 65\ M^{-1}$, were calculated.[4] The solvolysis product was 9-anisoylanthracene (**4**). The rearrangement of **2** gave mainly the ether **3** (S = Et) and its rate was slightly affected by added Bu_4NBr. The $k_{rear}(\mathbf{2})/k_t(\mathbf{1})$ value was 0.9.

The solvolysis of **1** in dry AcOH or in 1:1 AcOH-Ac_2O buffered with NaOAc gave mainly or exclusively the ketone **4**.[5] It was followed by UV or by bromide ion titration and was much slower than the loss of optical activity. The k_α/k_t values were 136 ± 1 in AcOH or in 1:1 AcOH-Ac_2O at 49.6 C. After 7 half-lives of the loss of optical activity, the main product was 10-acetoxy-9-(α-bromoanisylidene)-9,10-dihydroanthracene (**11**, S = Ac) and **4** constituted <2%.[6] The rearrangement of **2** in AcOH to the acetate **3** (S = Ac) was much faster than the solvolysis and was measured at a lower temperature. By applying a conservative value for the activation energy, a $k_{rear}(\mathbf{2})/k_t(\mathbf{1})$ value of >12 000 and a $k_{rear}(\mathbf{2})/k_\alpha(\mathbf{1})$ value of >150 in AcOH were estimated.

We interpret these results by a different solvolysis mechanism in the two solvents (Scheme I). **4** may be formed either via an initial C-Br bond cleavage (route a) or via an initial C-OH bond cleavage (route b). Optical activity is lost in either case since ions **5** and **10** are both achiral. Hence, the k_α/k_t probe for evaluating ion-pair return is meaningful only if route b is excluded. In 80% EtOH it is excluded by the common ion rate depression that shows that ≥87% **4** is derived from the *free* ion **5**,[7] by the similarity of k_t with the $k_t{}^\circ$ value of 1.8×10^{-4} s^{-1} for the solvolysis of **15** in 80% EtOH-2,6-lutidine at 105.1



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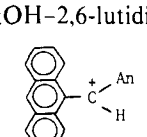

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°C[8] and by the much lower $k_{rear}(\mathbf{2})/k_t(\mathbf{1})$ value in 80% EtOH than in AcOH. Consequently, the near identity of k_α and k_t is due to a rate-determining formation of **5** which gives rapidly racemic products, and which returns to **1** with excess Br^-. As found in TFE,[1] ion-pair return with racemization (measured by $k_\alpha/k_t - 1$) is negligible. However, in the less ionizing and more nucleophilic 80% EtOH,[9] **5** shows lower selectivity in its reactions with Br^- and with the solvent.

The situation is different in AcOH and in 1:1 AcOH–Ac_2O. The high k_α/k_t values would usually be ascribed to ≥99% return with racemization of intermediate ion pairs,[2c] but this is in contrast with the results in TFE and in 80% EtOH and with the lower extent of ion-pair return (31% in 1:1 AcOH–Ac_2O and 47% in AcOH) in the solvolysis of (*Z*)-1,2-dianisyl-2-phenylvinyl bromide.[10] On the other hand, route b, with a rate-determining formation of **10,** accounts for the fact that formation of **11** precedes that of **4** with the ~3-fold higher k_α in AcOH compared with that in the much more ionizing TFE,[9] but it raises two problems: (a) it postulates racemization via capture of the hybrid ion **10a–b**[11] at C-10 rather than at C_α, although capture at C_α gives an aromatic system; (b) it has to explain the very high $k_{rear}(\mathbf{2})/k_\alpha(\mathbf{1})$ ratio which indicates that the ionization **2** → **16** is favored over the ionization **1** → **10,** although in the solvolytic generation of an sp^2-hybridized ion an α halogen is activating compared with an α hydrogen.[12] We ascribe the two phenomena to a steric interaction of the 1 and 8 hydrogens of the 9-anthryl group of the 9-anthrylmethyl cations **10** and **16** with the other α substituents.[13] A consequent loss of planarity, e.g., by rotation of the anthryl and/or the anisyl groups, results in destabilization of the ions which is higher for **16** (α-Br) than for **10** (α-H). The outcome is a higher k_{rear} for **2,** reduced importance of **10b** compared with **10a** and a lower rate of route b, steric hindrance to capture of C_α of **10,** and preferred capture by AcOH or AcO^- at C-10[5] to give **11.** Capture at C_α first gives **14** (S = Ac) which solvolyzes rapidly to give **4,** probably via **8** (S = Ac). Since the titrimetric k_t remains constant during a run and is identical with the values measured by UV, **4** is probably formed via the modified route b, **1** → **9** → **10** (→ **11** → **10**) → **14** → **8** → **4,** and not via **1** → **9** → **10** → **11** → **12** → **13** → **7** → **8** → **4.**

In conclusion, the solvolytic site of **1** in good-ionizing relatively nonacidic solvents (80% EtOH, TFE) is C_α, and C–Br bond cleavage is rate determining. In AcOH, the initial solvolytic site is C-10 and C–$^+OH_2$ and C–OAc bond cleavages are rate determining for the loss of optical activity and for the solvolysis, respectively. The mechanistic consequences are (i) the availability of an additional competing route to the several ones known for vinylic solvolysis,[14] and (ii) that the k_α/k_t probe for ion-pair return should not be used indiscriminately for vinylic systems.

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(4) The rate constants measured by UV were used for calculating α and *b*. By using α = 65 M^{-1}, we calculate that k_t should decrease by 4% at 1 half-life and by 6% at 2 half-lives owing to common ion rate depression. Such a decrease is within the experimental error.

(5) A minor product, which becomes the main product in wet AcOH/NaOAc, is 7-(9-anthryl)-7-bromoquinone methide, formed probably by attack of AcO^- on the methoxy group of **10.** This product was not formed in 1:1 AcOH–Ac_2O. Z. Rappoport, J. Greenblatt, and Y. Apeloig, *J. Org. Chem.*, in press.

(6) The product[5] and both k_α and k_t are sensitive to small amounts of water in the AcOH. The values given are for a single batch of AcOH.

(7) From Table I, the uncorrected $k_t°/k_d$ = 2.64 and ≥62% of **4** are derived from the free ion **5.** By correction for the normal salt effect, k_t = 3.33 × 10^{-4} s^{-1} with 0.1 M Bu_4NBr; i.e., $k_t°/k_d$ = 7.8 and ≥87% of **4** are derived from **5.**

(8) Y. Apeloig, Ph.D. Thesis, The Hebrew University, 1974.

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(13) Similar steric interactions were invoked for explaining the preferred formation of the 9-anthrylvinyl cation rather than the sp^2 α-(9-anthryl)-α-chloroethyl cation in the acetolysis of 9-(α-chlorovinyl)anthracene, and the relatively low solvolysis rate difference of the latter and α-(9-anthryl)ethyl chloride: Z. Rappoport, P. Shulman, and M. Thuval (Schoolman), *J. Am. Chem. Soc.*, **100,** 7041 (1978). The reaction of acetone at C_{10} of the 9-anthryl diphenylmethyl cation but at C_α of the 9-anthryl phenylmethyl cation (B. Bodo, J. Andrieux, and D. Molho, *C.R. Acad. Sci., Paris, Ser. C,* **273,** 170 (1971)) may be due to a similar reason.

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Transient Photocurrents and Conversion Losses in Polysulfide-Based Photoelectrochemical Cells

Sir:

The development of a practical photoelectrochemical cell (PEC) for solar energy conversion into electricity requires long-term output stability and reasonable conversion efficiency. Treatments have been presented which can predict the thermodynamic stability of a certain semiconductor/electrolyte combination,[1] but, even if a system is thermodynamically unstable, kinetic factors may still lead to long-term stability.[2] Transient photocurrents, as reported by us recently,[3] can be useful in certain cases, to evaluate PEC performance by way of the, somewhat neglected, effect of the cell's solution kinetics.

We describe here how such transients yield information on long-term stability and conversion efficiency losses in PEC's using polychalcogenide redox electrolytes. Figure 1 illustrates the time dependence of the photocurrent (at close to short circuit conditions) in a PEC comprising a thin-layer, polycrystalline CdSe photoelectrode and polysulfide redox electrolyte.[4] The transient photocurrent can be analyzed by considering the difference between the peak-current density (I_p) and the steady-state one (I_s), and by defining a normalized ratio (NR) ≡ $(I_p - I_s)/I_p$. As $(I_p - I_s)$ expresses conversion losses in the cell, NR = 0 represents zero loss and NR = 1 total loss, i.e., a situation with no steady-state output.

To gain insight in the cause of these transients, the NR was investigated as a function of several solution parameters (Figure 2). (Not shown are effects of temperature or peak-

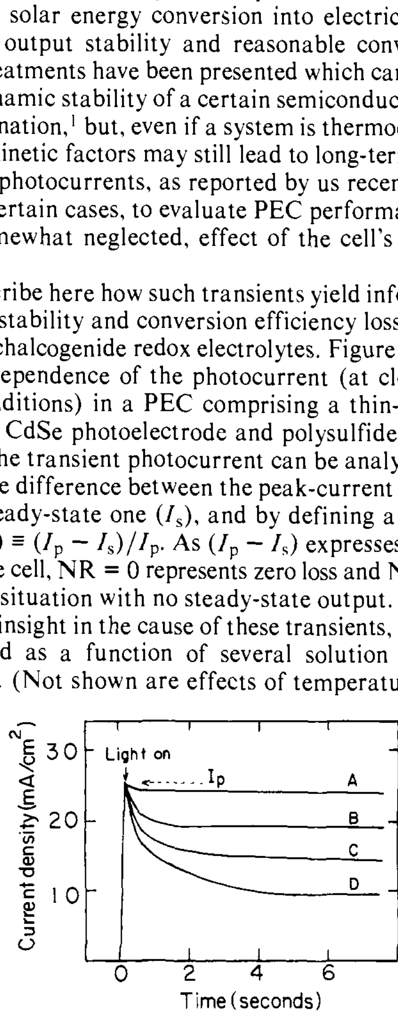

Figure 1. Scheme of photocurrent density vs. time in *n*-CdSe/polysulfide/CoS PEC. Electrolyte composition: A, 0.9 M [S^{2-}], no OH^-, 6.10^{-3} M [Se^{2-}], temp, 34 °C, NR, 0.05 (the same behavior is obtained in 2 M [S^{2-}], 2 M [S], 2 M [OH^-], no Se^{2-}); B, 0.9 M [S^{2-}], 1 M [S], no OH^-, no Se^{2-}, temp, 34 °C, NR, 0.2; C, 0.25 [S^{2-}], 0.2 M [S] no OH^-, no Se^{2-}, temp, 44 °C, NR, 0.4; D, as C but at 24 °C, NR, 0.6. Identical peak current densities (I_p) were obtained in all cases by adjusting the incident light intensity; a 2-cm^2 area of polycrystalline thin layer of CdSe on Ti was exposed to light and solution. Light source: filtered 250-W quartz-iodine lamp (λ >610 nm only). Care was taken to ensure that the counter electrode[3a] was negligibly polarized, so that no part of the transient response ascribed to the CdSe could be due to such polarization.

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