

STERIC EFFECTS IN THE ELECTROREDUCTION OF 9-ANTHRYL STYRYL KETONE AND 9,10-ANTHRYL BIS(STYRYL KETONE)

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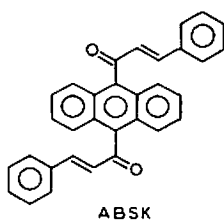
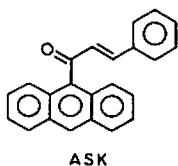
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ABSTRACT

The electrochemical behavior of 9-anthryl styryl ketone (ASK) and 9,10-anthryl bis(styryl ketone) (ABSK) in acetonitrile and N,N-dimethylformamide at a Pt electrode was investigated by cyclic and rotating ring disk electrode (RRDE) voltammetry and controlled potential coulometry. ASK is reduced in a reversible one-electron step to form the radical anion which rapidly couples ($k_2 = 10^5 M^{-1} s^{-1}$) to form the dimeric dianion. The dimer can be reoxidized to form ASK. ABSK is reversibly reduced to the stable dianion which shows no tendency to couple. The cyclic voltammogram wave shape suggests that the styryl-keto groups in the 9- and 10-positions are non-interacting so that the reduction occurs in two steps whose standard potentials differ by the statistically predicted 36 mV.

Previous papers from this laboratory and elsewhere have dealt with steric effects on the electrochemical behavior of substituted anthracenes and olefins and the reactions of the radical ions derived from these (see e.g., refs. 1-6 and references therein). Thus, for example, the rate of dimerization of the radical anions derived from the *cis*-form dialkyl-maleates was found to be much larger than that of the corresponding *trans*-form dialkyl-fumarates [4,6], with the rates also depending upon the size of the alkyl group [5,6]. In addition the potential for reduction of substituted anthracenes was shown to depend upon steric interactions affecting the planarity of the molecule and the extent of resonance interaction of the substituents with the anthracene nucleus [1]. We thought it of interest to extend these studies to two molecules which have features of both activated olefins and substituted anthracenes which have recently been described [7], 9-anthryl styryl ketone (ASK) and 9,10-anthryl bis(styryl ketone) (ABSK).



Studies of these by cyclic voltammetry, controlled potential coulometry, and rotating ring disk electrode (RRDE) experiments in acetonitrile (ACN) and N,N-dimethylformamide (DMF) solutions demonstrate that the large steric interactions in these molecules greatly affect their electrochemical behavior.

EXPERIMENTAL*Chemicals*

The preparation and purification of ASK and ABSK was carried out following a previously described procedure [7]. Tetra-n-butylammonium perchlorate (TBAP), used as a supporting electrolyte for all experiments, was of polarographic grade and purchased from Southwestern Analytical Chemicals (Austin, Texas). The TBAP was dried under vacuum at 100°C for 2 days then stored in an inert atmosphere. The procedures for purification of the solvents ACN and DMF have been previously described [8,9].

Apparatus and procedure

The electrochemical cell used for cyclic voltammetry is shown in Fig. 1. The working electrode was a platinum disk (0.038 cm²) sealed in soft glass. Pretreat-

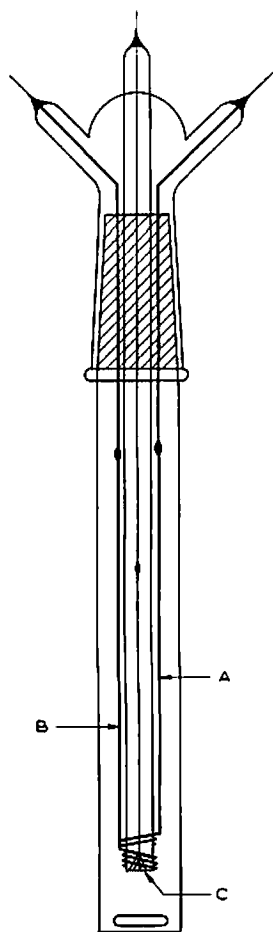


Fig. 1. Electrochemical cell for voltammetric measurements. (A) Pt wire auxiliary electrode; (B) Ag wire reference electrode; (C) Pt disk (sealed in glass) working electrode.

ment of this electrode consisted of polishing with alumina slurry (0.3 μm particle size) on a felt cloth. The auxiliary electrode was a platinum wire and the quasi-reference electrode was a silver wire. The potential of this reference was determined following each series of experiments by adding 9,10-diphenylanthracene and observing the voltammetric behavior of this species, whose reversible potential in ACN or DMF is known with respect to an aqueous saturated calomel electrode (SCE). For coulometric measurements a standard three compartment cell was used [10].

All the solutions were prepared in a glove-box (Vacuum Atmospheres Company, Hawthorne, Calif.) equipped with a Model MO-40-1 Dri-Train. Cyclic voltammetric and coulometric measurements were carried out in the glove-box with a PAR Model 173 potentiostat incorporating a Model 179 digital coulometer and equipped with positive feedback for $i-R$ compensation, and a Model 175 universal programmer (Princeton Applied Research Corporation, Princeton, N.J.). The current-potential ($i-E$) curves were recorded on a Houston Instruments Model 2000 XY recorder (Houston Instruments, Austin, Texas). For scan rates higher than 500 mV s^{-1} , the current-voltage curves were recorded on a Tektronix Type 564 storage oscilloscope.

The cell used for RRDE experiments was described earlier [11]. For the RRDE measurements a Tacussel Electronique potentiostat Model BIPAD-2 was used. A Wavetek function generator provided the potential ramp and a Mosely Model 7100 B dual pen strip chart recorder was used to record the ring and disk current simultaneously.

RESULTS

9-Anthryl styryl ketone

The cyclic voltammetry (c.v.) of a solution containing 2.0 mM ASK and 0.1 M TBAP in ACN at low scan rates showed one reduction wave at -1.48 V vs. SCE with an oxidation wave at -0.52 V on scan reversal (Fig. 2A). Although no anodic reversal wave was found at potentials of the first reduction wave at low scan rates, an appreciable oxidation current appeared on sweep reversal at scan rates above 5 V s^{-1} (Fig. 3). Typical data for c.v. are shown in Table 1. The ratio of the cathodic peak current to the square root of the scan rate, $i_{pc}/\nu^{1/2}$, decreased with increasing scan rate. Treatment of the cyclic voltammetric data using the method developed by Olmstead et al. [22] produced results which agreed with their predictions for an electrochemically initiated dimerization reaction.

Controlled potential coulometry of a 4.74 mM ASK -0.1 M TBAP solution at a Pt electrode held at -1.6 V gave $n_{app} = 0.95$ (where n_{app} is the number of electrons per molecule). The initial color of the solution was yellow; following reduction the solution had a dark red color which did not change on standing for several days. The c.v. of the solution after reduction showed an irreversible oxidation wave at about -0.5 V ; the height of this wave was about one-half that of the original reduction wave (Fig. 2B). Controlled potential oxidation of the reduced species at 0.0 V resulted in an n_{app} value of 0.89. C.v. following this oxidation produced $i-E$ curves which were located at potentials essentially identical to that of the original solution containing parent compound, although the

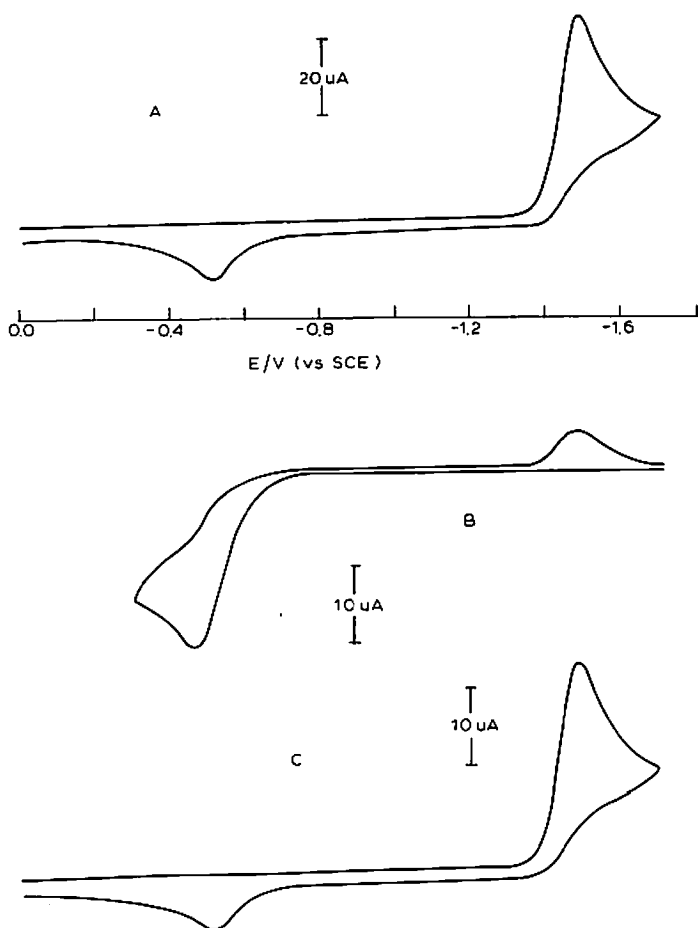


Fig. 2. Cyclic voltammogram of 2.0 mM ASK in 0.1 M TBAP-ACN, scan rate 0.2 V s^{-1} . (A) Before coulometric reduction, (B) after coulometric reduction at -1.6 V (scanned from this potential in a positive direction), (C) after reoxidation at 0.00 V .

waves were somewhat diminished in height (Fig. 2C). The above results suggest a mechanism which involves an initial one electron transfer to form a radical anion followed by a rapid dimerization to form a species which can be oxidized back to the original compound:



These results resemble those obtained for the reduction of quinoline in liquid ammonia which also involved radical anion formation and formation of a dimeric species which could be oxidized back to the parent [12]. The i_{pa}/i_{pc} c.v. behavior of the 2.0 mM ASK solution suggests a radical ion half-life of about 5 ms or a dimerization rate constant, k_2 , of about $10^5 \text{ M}^{-1} \text{ s}^{-1}$.

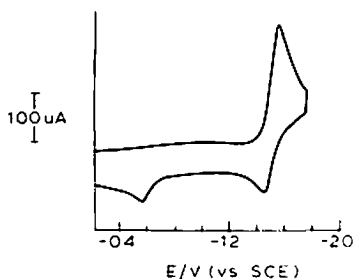


Fig. 3. Cyclic voltammogram of 2.0 mM ASK in 0.1 M TBAP-ACN, scan rate 20 V s^{-1} .

To confirm this mechanism and obtain a more precise value for k_2 , RRDE experiments were undertaken. As in previous studies [4,5,11,13–15] the variation of the collection efficiency, N_k :

$$N_k = |i_r/i_d| \quad (4)$$

(where i_r and i_d are the ring and the disk currents, respectively) as a function of the disk current, at several values of the rotation rate, ω , was determined. As before i_d was expressed in terms of the fraction of the limiting disk current of the reduction wave, $i_{d,l}$:

$$CONI = i_d/i_{d,l} \quad (5)$$

RRDE voltammetry showed a single reduction wave when the disk potential was scanned toward negative values. The i_r value was determined for various values of i_d with the ring held at potentials at the foot of this wave. Typical results are shown in Fig. 4. The upward trend in N_k values with l -CONI is characteristic of a dimerization reaction, as opposed, for example to a reaction scheme involving solely first-order decay of the product or coupling of product with parent [13]. To obtain a good fit to the data and account for the rather gradual

TABLE 1

Cyclic voltammetric data for reduction of 9-anthryl styryl ketone in ACN^a

Abbreviations: i_{pc} = cathodic current; i_{pa} = anodic current; E_{pc} = cathodic peak potential. Current function, $i_p/v^{1/2}c = 31 (\text{A s}^{1/2} \text{ cm}^3)/(\text{V}^{1/2} \text{ mol})$

Scan rate, v/Vs^{-1}	$i_{pc}/\mu\text{A}$	i_{pc}/i_{pa}	$-E_p/\text{V vs. SCE}$
0.05	16	—	1.48
0.1	23	—	1.48
0.2	33	—	1.48
0.5	42	—	1.51
1.0	58	—	1.52
5	123	0.29	1.53
10	173	0.30	1.56
20	242	0.42	1.56
50	362	0.44	1.58

^a Solution contained 2 mM ASK and 0.1 M TBAP.

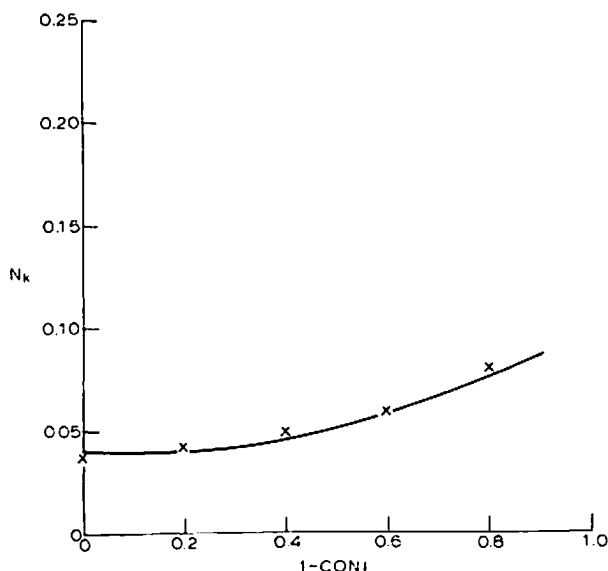


Fig. 4. Collection efficiency of the radical anion of ASK (\times), 0.75 mM in 0.1 M TBAP-DMF solution for the ring electrode maintained at a potential of -0.80 V vs. SCE. Rotation rate, ω , 98.5 radians/s. The solid line is the simulated result for $XKT = 1.5$, $XKTC = 10$ (corresponding to $k_1 = 11 \text{ s}^{-1}$ and $k_2 = 10 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).

change of N_k with $CONI$, a contribution of a parallel first-order reaction of ASK^- , reaction (6) had to be included in digital simulations [15], carried out in terms



of the kinetic parameters XKT and $XKTC$:

$$XKT = (0.51)^{-2/3} (\nu/D)^{1/3} \omega^{-1} k_1 \quad (7)$$

$$XKTC = (0.51)^{-2/3} (\nu/D)^{1/3} \omega^{-1} c k_2 \quad (8)$$

where ν is the kinematic viscosity, c is the concentration of ASK, and D is the diffusion coefficient, assumed to be equal for all species. The diffusion coefficient for ASK used in the above equations was determined by c.v. and potential step experiments to be $1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C by the method outlined by Adams [16].

9,10-Anthryl bis(styryl ketone)

A cyclic voltammogram of a solution containing 2.6 mM ABSK and 0.1 M TBAP in ACN is shown in Fig. 5 and data for scan rates of 50 mV s^{-1} to 500 mV s^{-1} are summarized in Table 2. The cathodic and anodic peak potentials, E_{pc} and E_{pa} , respectively, the current function, and the ratio i_{pa}/i_{pc} , were essentially independent of scan rate; this behavior is generally characteristic of a system which involves rapid (Nernstian) electron transfer to produce a stable product.

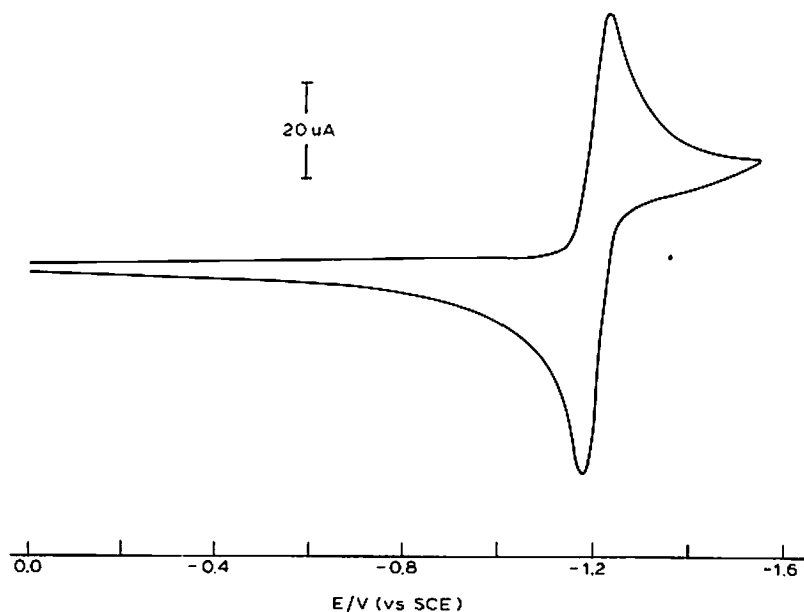


Fig. 5. Cyclic voltammogram of 2.64 mM ABSK in 0.1 M TBAP-ACN, scan rate 0.2 V s^{-1} .

The current ratio i_{pa}/i_{pc} was slightly larger than one, implying some adsorption of the product on the electrode surface; similar behavior has been observed for the second reduction wave of nitrobenzene in liquid ammonia [10]. Controlled potential electrolysis at -1.4 V resulted in an intense blue solution and an n_{app} value of 2.0. C.v. of the solution following reduction showed only the original reversible waves. Coulometric oxidation of the product at -0.8 V gave $n_{app} = 1.8$ and produced a solution with the color of the original compound. The c.v. following this oxidation was essentially the same as that of the original solution. These results are consistent with the reduction of ABSK in an overall two-electron reaction.

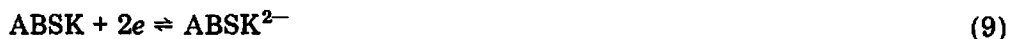


TABLE 2

Summary of c.v. parameters for the reduction of 9,10-anthryl bis(styryl ketone) in ACN

$E_{pc}/\text{V vs. SCE}$	-1.22
$\Delta E_p = (E_{pa} - E_{pc})/\text{mV}$	55 ± 5
i_{pa}/i_{pc}	1.12 ± 0.04
Current function ^a	44
Diffusion coefficient ^b $\text{cm}^2 \text{ s}^{-1}$ at 25°C	5.8×10^{-6}

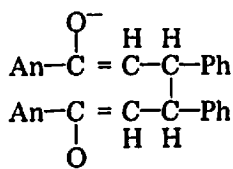
^a $i_p/v^{1/2} c = (\text{A s}^{1/2} \text{ cm}^3)/(\text{V}^{1/2} \text{ mol})$.

^b Calculated from the current function assuming $n = 2$.

DISCUSSION

ASK

The reduction mechanism of ASK appears to follow that of a deactivated olefin, with coupling probably occurring at the carbon β to the carbonyl group yielding the dimer shown below. Coupling at the carbonyl carbon to form the pinacol is unlikely, because this



site is essentially blocked by the neighboring anthracene group. Even coupling at the β -carbon is quite hindered sterically, and hence the observed coupling rate compared to other related olefins (e.g., fumarates [3,4,6,11], dibenzoyl ethylene [3,17], benzalacetophenone [18]) seems unusually large. A possible reason for this large rate could involve the configuration near the double bond. From X-ray crystallography studies [19] it is known that the styryl-keto group is rotated almost completely (ca. 80°) out of the plane of the anthracene ring; little delocalization is expected into the anthracene. The strain may cause a greater amount of odd electron delocalization on to the β -carbon following the formation of the radical anion. An analogous type of argument has been used to justify the faster coupling rates of *cis*-radical anions compared to the *trans*-forms upon reorganization following electron transfer [3,4,14]. The dimeric dianion apparently does not protonate rapidly and dissociates upon oxidation. The detailed nature of this anodic reaction was not investigated.

ABSK

The results for ABSK are very different than those of ASK. The $i_{p,c}$ value from c.v. and the coulometry results clearly point to a two electron reaction. The wave shape and the ΔE_p value, which are close to those expected for a one-electron wave, suggest that the reduction occurs in two, closely spaced, one-electron waves:



The effect of structure on the potentials for successive electron transfers has been considered previously [20,21]. As pointed out by Ammar and Savéant [20], if a molecule contains two identical non-interacting groups, and there is no significant reorganization or solvation change upon electron transfer, the addition of electrons to the groups will follow simple statistics, and will result in a splitting between E_1° and E_2° given by

$$E_1^\circ - E_2^\circ = (RT/F) \ln 4 = 36 \text{ mV} (25^\circ\text{C}) \quad (12)$$

This spacing will result in a voltammetric wave which is indistinguishable from

a reversible one-electron one. ABSK appears to show this behavior.

Although the structural formula might make it appear that there is considerable conjugation between the two styryl-keto groups, a molecular model or the previously mentioned X-ray crystallography study make it clear that these groups are rotated completely out of the plane of the anthracene ring and there is apparently no interaction between them. The lack of dimerization for the case of ABSK (as compared to ASK) can be attributed to the increased overall charge on the molecule causing electrostatic repulsion between approaching dianions as well as the increased steric effects caused by the additional styryl-keto group.

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