Reactions of Aromatic Radical Anions. VI.[1] Kinetic Study of the Reaction of Sodium Naphthalene with Water[2a]

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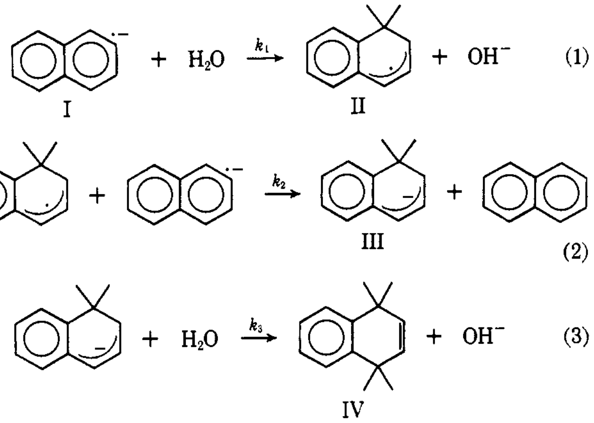
Abstract: Using a modified rapid-mixing stopped flow device a kinetic study of the reaction of sodium naphthalene with water has been performed. The rate law has been established to be $-d[\text{Nap}\cdot^-]/dt = 2k_1[\text{Nap}\cdot^-][H_2O]$, with a value of k_1 at 20° of $1.01 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ in tetrahydrofuran. Moreover, the reaction of the dihydronaphthyl anion, an intermediate in the overall reaction, with water is considerably faster than that of the radical anion. Activation parameters and the deuterium kinetic isotope effect have been determined. Finally, a determination of the effect of the state of aggregation upon reactivity by solvent variation has been performed. The resulting conclusions are diverse. First, the Paul, Lipkin, and Weissman mechanism is in full agreement with the rate law. Second, the reactivity of sodium naphthalene toward a proton source is significantly less than that of a structurally related anion. Third, the transition state occurs very early with little carbon–hydrogen bond formation. Finally, the reactivity of tight ion pairs is greater than that of solvent-separated ion pairs. The discussion includes the implications of these findings to other aromatic radical anion reactions and their general reactivity patterns.

Mechanistic studies of the chemistry of aromatic radical anions have relied for the most part upon product structure and competition experiments.[1,3–5] Moreover, kinetic studies, usually the most powerful mechanistic tool, have been confined to electron spin resonance (esr) rate studies of electron exchange[6] and conventional rate studies of very slow reactions,[7] with the interesting exception of pulse radiolysis studies of aromatic radical anions in aliphatic alcohols.[8] It is not surprising that the high chemical reactivity and air and moisture sensitivity of these reagents have impeded rate studies in the required low concentrations.

However, within the past few years the application of rapid mixing stopped-flow techniques to the studies of carbanions has proven enormously successful,[9] and encouraged by these studies we have sought to adapt this basic design[10] to the special requirements of aromatic radical anions. The reaction of water with sodium naphthalene was selected for initial study because it is a reaction in which the initial step involves sodium naphthalene acting exclusively as a base, and hence comparison with other bases is facilitated, and because the mechanism of this reaction is probably better understood than most radical anion reactions. The Paul, Lipkin, and Weissman mechanism,[11] involving the sequence of steps shown in eq 1–3 (counterions have been omitted), has been verified experimentally.[3b] Accordingly, this reaction



affords an opportunity not only to test both the new apparatus and the accepted mechanism, but also to probe several subtle kinetic questions. These include the question of the intermediacy of species III, the nature of the rate-determining step, and finally the effect of the state of aggregation of the radical anion on the chemical reactivity. This paper reports the results of this investigation in two parts. The first part deals with the kinetics and mechanism and the second part deals with the effect of the state of aggregation on reactivity.

Results and Discussion

The Rate Law. The kinetic expression for the rate of loss of naphthalene radical anion (I) [Nap·⁻] for the

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(1) Previous paper in this series: S. Bank and J. Bank, *Tetrahedron Lett.*, 4533 (1969).

(2) (a) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstracts ORGN-32; (b) NDEA Title IV Fellow.

(3) (a) S. Bank, T. A. Lois, and M. C. Prislopski, *J. Amer. Chem. Soc.*, **91**, 5407 (1969); (b) S. Bank and W. D. Closson, *Tetrahedron Lett.*, 1349 (1965).

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(5) (a) G. Levin, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **92**, 2268 (1970); (b) W. D. Closson, S. Ji, and S. Schulenberg, *ibid.*, **92**, 650 (1970).

(6) (a) R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957); (b) R. Chang and C. S. Johnson, Jr., *ibid.*, **88**, 2338 (1966); (c) K. Hofelmann, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 4645 (1969), and references cited therein.

(7) (a) J. T. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969); (b) E. Warhurst and R. Whittaker, *Trans. Faraday Soc.*, **62**, 707 (1966), and earlier papers in this series.

(8) (a) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, 41, 2190 (1964); (b) S. Arai, E. L. Tremba, J. R. Brandon, and L. M. Dorfman, *Can. J. Chem.*, **45**, 1119 (1967); (c) L. M. Dorfman, *Accounts Chem. Res.*, 3, 224 (1970).

(9) (a) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 2960 (1967); (b) C. D. Ritchie and R. E. Uschold, *ibid.*, **90**, 2821, 3415 (1968); (c) T. E. Hogen-Esch and J. Smid, *ibid.*, **89**, 2764 (1967).

(10) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).

(11) D. E. Paul, P. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

Paul, Lipkin, and Weissman mechanism is given by

$$-\frac{d[\text{Nap}\cdot^-]}{dt} = k_1[\text{H}_2\text{O}][\text{Nap}\cdot^-] + k_2[\text{NapH}\cdot][\text{Nap}\cdot^-] \quad (4)$$

where NapH· is species II in eq 1. This expression can be simplified since electron transfer from a radical ion to a radical is known to be very fast.[4d,5a,11] Moreover, reaction times will be much larger than $1/k_2$ since $k_2 \geqq 10^8\ M^{-1}\ \text{sec}^{-1}$. These conditions are necessary and sufficient for the steady-state assumption for the species NapH·. Accordingly, we have

$$\frac{d[\text{NapH}\cdot]}{dt} = k_1[\text{H}_2\text{O}][\text{Nap}\cdot^-] - k_2[\text{NapH}\cdot][\text{Nap}\cdot^-] = 0 \quad (5)$$

and

$$[\text{NapH}\cdot] = \frac{k_1[\text{H}_2\text{O}]}{k_2} \quad (6)$$

Substitution of eq 6 into eq 4 leads to

$$-\frac{d[\text{Nap}\cdot^-]}{dt} = 2k_1[\text{H}_2\text{O}][\text{Nap}\cdot^-] = 2k_1'[\text{Nap}\cdot^-] \quad (7)$$

where

$$k_1' = k_1[\text{H}_2\text{O}]$$

Thus, the expected kinetics are overall second order, first order in water and first order in the naphthalene radical anion, and the observed second-order rate constant is equal to twice the rate of the initial protonation step.

That the reaction obeyed second-order kinetics was established in two ways. First, with an excess of water present the reaction gave a good linear plot for first order (Figure 1) and, equally important, Table I records the second-order rate constants as a function of water concentration. With a variation of water concentration over an order of magnitude the same rate constant was obtained within the experimental accuracy. Second, the observed pseudo-first-order rate constants at a given water concentration excess are independent of the initial sodium naphthalene concentration as shown in Table II.

Table I. Rate Constants for the Reaction of Sodium Naphthalene with Water at 20°

Water concn × 10^2	k, M^{-1} $\text{sec}^{-1} \times 10^{-4}$
0.92	0.80[a]
2.29	1.20[a]
1.79	1.10[a]
1.72	0.92[a]
1.82	0.0195[b,c]
13.2	0.0234[b]

[a] For sodium naphthalene in tetrahydrofuran with concentration of 0.42–1.45 × 10^{-4} M. [b] For sodium naphthalene in tetrahydrofuran–tetraglyme with concentration of 1.1–6.2 × 10^{-4} M. [c] For slow portion of the curve.

Table II. Pseudo-First-Order Rate Constants for the Reaction of Sodium Naphthalene and Water in THF at 20.0° at Constant [H_2O]

$[\text{Nap}\cdot^-]_{\text{init}} \times 10^4\ M$	$[\text{H}_2\text{O}] \times 10^2\ M$	k^1,[a] sec^{-1}
0.235	1.15	295
0.605	1.15	284
0.130	0.86	160.0
0.430	0.86	166.0
0.099	0.90	197.0
0.274	0.90	190.2

[a] Pseudo-first-order rate constant, k_1' in eq 11.

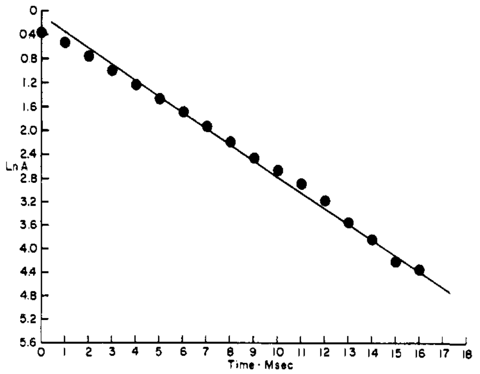

Figure 1. Pseudo-first-order plot for the disappearance of sodium naphthalene in THF reacting with an excess of water in THF at 20.0°.

Turning attention to the expression for the rate of product formation, we have from eq 3

$$\frac{d[\text{NapH}_2]}{dt} = k_3[\text{NapH}\cdot^-][\text{H}_2\text{O}] \quad (8)$$

where $NapH_2$ is species IV in eq 3 and $NapH^-$ is species III in eq 2. For $NapH^-$ we have

$$\frac{d[\text{NapH}^-]}{dt} = k_2[\text{Nap}\cdot^-][\text{NapH}\cdot] - k_3[\text{NapH}^-][\text{H}_2\text{O}] \quad (9)$$

and by substitution of eq 6 we obtain

$$\frac{d[\text{NapH}^-]}{dt} = k_1[\text{Nap}\cdot^-][\text{H}_2\text{O}] - k_3[\text{NapH}^-][\text{H}_2\text{O}] \quad (10)$$

With an excess of water this reduces to

$$\frac{d[\text{NapH}^-]}{dt} = k'[\text{Nap}\cdot^-] - k_3'[\text{NapH}^-] \quad (11)$$

where k_1' and k_3' are the respective pseudo-first-order rate constants for the protonation of the radical anion and anion as defined by eq 7. The concentration of $NapH^-$ at any time is therefore given by

$$[\text{NapH}^-] = \frac{[\text{Nap}\cdot^-]_0 k_1'}{k_3' - k_1'}[e^{-k_1't} - e^{-k_3't}] \quad (12)$$

where $[\text{Nap}\cdot^-]_0$ is the initial concentration of naphthalene radical anion. The time at which the concentration of $NapH^-$ is at a maximum ($t_{\max}$) is

$$t_{\max} = \frac{1}{k_3' - k_1'} \ln \frac{k_3'}{k_1'} \quad (13)$$

Substitution of eq 13 into eq 12 leads to this expression for the maximum concentration of $NapH^-$ ($[\text{NapH}^-]_{\max}$)

$$[\text{NapH}^-]_{\max} = [\text{Nap}\cdot^-]_0 \frac{k_1'}{k_3' - k_1'}\left[\left(\frac{k_3'}{k_1'}\right)^{\frac{k_1'}{k_1' - k_3'}} - \left(\frac{k_3'}{k_1'}\right)^{\frac{k_3'}{k_1' - k_3'}}\right] \quad (14)$$

If we set $k_3' = ak_1'$, where a is some constant, then eq 14 reduces to

$$[\mathrm{NapH^-}]_{\max} = \frac{[\mathrm{Nap}\cdot^-]_0}{a-1}[a^{1/(1-a)} - a^{a/(1-a)}] = [\mathrm{Nap}\cdot^-]_0 a^{a/(1-a)} \quad (15)$$

From eq 15 it is shown that the maximum NapH$^-$ concentration will be a fraction of the initial Nap$\cdot^-$ concentration that depends on the value of the rate ratio (a). Our monitoring system could easily detect NapH$^-$ corresponding to 10% of the initial Nap$\cdot^-$ concentration. Substitution of this value into eq 15 reveals that the corresponding value of a is 5. Accordingly, if $k_3 \leqq 5k_1$ we can detect the presence of NapH$^-$.

Equally important, the time of the maximum concentration of NapH$^-$ is also a function of a. Upon substitution of a into eq 13 we obtain

$$t_{\max} = \frac{1}{k_1'(a-1)} \ln a \quad (16)$$

With a water concentration of 1×10^{-2} M the value of k_1 is 1.01×10^2 sec^{-1}. Combining this with the just detectable value of a of 5 the maximum concentration of NapH$^-$ would occur at 4 msec. This corresponds to a time well within the first half-life of the first step and therefore would be seen readily. In conclusion, with regard to both concentration and time, the experimental system can confidently detect $k_3/k_1 \leqq 5$.

Dihydronaphthyl Anion (III). To provide an accurate base for detecting the anion during the course of the reaction, the anion was synthesized by an independent route. In the first attempt, butyllithium was allowed to react with 1,4-dihydronaphthalene in tetrahydrofuran (THF). The uv spectrum had a band centered at 400 mμ, but the spectrum disappeared with time. A possible explanation for this phenomenon is anionic polymerization of isomerized dihydronaphthalene, and accordingly a sample of water-quenched product was analyzed for molecular weight by osmometry. The average molecular weight of 1500 indicates that polymerization had indeed occurred.

A more successful generation of the anion was achieved by the addition of a deficiency of water to a dilute solution of sodium naphthalene in THF. The resulting spectrum had a peak at 433 mμ, and no absorptions of sodium naphthalene (vide infra) were present. The minimum extinction coefficient, calculated by the assumption that [NapH$^-$] is one-half the initial [Nap$\cdot^-$], is equal to $\epsilon = 1.08 \times 10^4$ M^{-1} cm^{-1}. This value compares with those for 1-phenyl-2-propenyllithium $\lambda_{\max}$ 395 mμ (log ϵ 4.38),[12] and that of the same anion obtained on a solid support, $\lambda_{\max}$ 435 mμ.[13]

The absorption of sodium naphthalene in THF agreed with the literature values[11] for the principal maxima at 365 and 765 mμ with ϵ 5250 and 2250, respectively. At 435 mμ the value of the extinction coefficient is ~3200, or about three times greater than that for the radical anion. Therefore, an anion concentration of ~10% of the initial radical anion would result in demonstrably slower kinetics at this wavelength.

Table III. Second-Order Rate Constants for the Reaction of Sodium Naphthalene and Water in THF Measured at Different Wavelengths[a]

T, °C	$\lambda_{\max}$, mμ	k_1,[a] M^{-1} sec^{-1} $\times 10^{-3}$
25.0	365	13.1 ± 3.4
	435	14.0 ± 2.8
15.0	365	6.94
	405	7.62 ± 0.36
1.0	365	1.65 ± 0.64
	440	2.28 ± 0.17

[a] For sodium naphthalene in tetrahydrofuran with concentration of 0.37–1.95 $\times 10^{-5}$ M.

Table III records the values for the second-order rate constants at the two wavelengths at several temperatures. Of critical importance, the measured rate constant at 435 mμ is not smaller than the value obtained at 365 mμ, but in fact always somewhat larger, but within the experimental accuracy. Finally, the dihydronaphthyl anion has essentially no absorption at 765 mμ. Accordingly, reaction rates studied at 765 mμ monitor only the disappearance of sodium naphthalene. Rates determined at this wavelength also agree with those found at 435 mμ. We may conclude confidently that $k_3/k_1 > 5$ and since our calculations were based on conservative estimates we feel the value is considerably greater. The anion concentration does not exceed 10^{-5} M during reaction.

Turning attention now to the kinetic expressions, with $k_3 > k_1$, we can apply the steady-state assumption to eq 11 and solve for [NapH$^-$]

$$[\mathrm{NapH^-}] = \frac{k_1'[\mathrm{Nap}\cdot^-]}{k_3'} \quad (17)$$

Substitution of eq 17 into (8) yields

$$\frac{\mathrm{d}[\mathrm{NapH_2}]}{\mathrm{d}t} = k_1'[\mathrm{Nap}]\cdot^- = k_1[\mathrm{Nap}\cdot^-]\mathrm{H_2O} \quad (18)$$

The overall rate expression is therefore

$$\frac{-\mathrm{d}[\mathrm{Nap}\cdot^-]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Nap}]}{\mathrm{d}t} + \frac{\mathrm{d}[\mathrm{NapH_2}]}{\mathrm{d}t} \quad (19)$$

and with

$$\frac{\mathrm{d}[\mathrm{Nap}]}{\mathrm{d}t} = k_1[\mathrm{Nap}\cdot^-][\mathrm{H_2O}] \quad (20)$$

and eq 18 we obtain

$$\frac{-\mathrm{d}[\mathrm{Nap}\cdot^-]}{\mathrm{d}t} = 2k_1[\mathrm{Nap}\cdot^-][\mathrm{H_2O}] \quad (21)$$

The kinetic study is fully consistent with the accepted mechanism.

Comparison of Protonation Rates. The implication that the relative magnitudes of k_1 and k_3 represent protonation of two very different kinds of basic species requires a comparison with related systems, and an account for the differences in affecting subsequent chemical reactivity.

The value of k_1 may be compared with the value for the first-order decay of naphthalene radical anion generated by pulse radiolysis in aliphatic alcohols. In isopropyl alcohol at 25° the value is 4.4×10^4 M^{-1} sec^{-1}.[8b] In this work at 25° we obtain a value for k_1 of

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[12] R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, **85**, 1651 (1963).

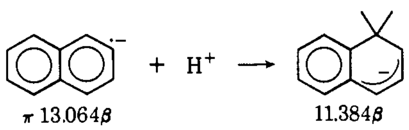
[13] M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *ibid.*, **91**, 6505 (1969).

$1.35 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. Interestingly, the rates are of comparable magnitude despite the important differences in the systems. To some extent this is misleading, and a fuller discussion of a comparison between these two systems may be found in the section on activation parameters.

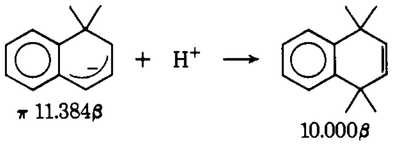
The value of k_3 may be compared with protonations of other anions. The only relevant system that we are aware of is the trityl anion. Ritchie has estimated the rate constant for the protonation of the trityl anion by methanol in methanol solution to be $10^8\ M^{-1}\ \text{sec}^{-1}$.[9b] We would expect protonation of the cinnamyl-type ion (III) to be as fast or faster since dihydronaphthalene has an estimated pK of ~35,[14] about six units greater than triphenylmethane. Although extrapolation from methanol to tetrahydrofuran solution and from methanol to water as protonating agents is well beyond present day capabilities, our estimate that $k_3 > 10^4\ M^{-1}\ \text{sec}^{-1}$ is compatible.

We account for the observation that protonation of a radical anion is significantly slower than protonation of a structurally related anion by two types of calculations, localization energies for the protonation of both species, and changes in bond order for both systems.

From published[15] values for the energy levels for protonation of naphthalene radical anion



$\Delta\pi$ is 1.680β. For the anion protonation we have



with a $\Delta\pi$ of 1.384β. The difference in localization energies is ~0.3β with the anion being favored. Using the value of $\beta = 35$ kcal/mol for localization reactions,[16] and a Brønsted slope of 0.5, the predicted kinetic reactivity of the anion is 10^3–10^4 greater than that of the radical anion, which is consistent with our experimental results.

The principle of least motion[17] has been advantageously applied to anion protonations.[18] For this purpose, the sum of the squares of the bond order changes for the several protonations have been calculated. For naphthalene radical anion the value is 0.726 whereas the values for the anion are 0.696 and 0.716 for the 1,4- and 1,2-dihydro products, respectively. A crude estimate of the relationship between bond order changes and reactivity can be obtained from product studies of the anion protonation. Under conditions that minimize isomerization the product ratio of 1,4- to 1,2-dihydronaphthalene is ~100:1.[19] Since this corresponds to a difference in bond order terms of 0.02, protonation of the radical anion is estimated to be 150 times slower than the anion. In sum, both types of calculations lead to predictions in accord with the experimental observations.

Our understanding that the radical anion is an enormously weak base and a poor nucleophile explains some heretofore surprising chemical results. For example, alkylation products of naphthalene radical anion form by radical coupling rather than by displacement reactions.[4b,c,20] Since radical anions have another reaction path available, namely electron transfer, it is not surprising that they behave as reducing agents rather than as bases. In addition, although highly reactive, radical anions are stable in ether solvents, and perhaps in even more strongly acidic solvents.

Product Studies. The materials resulting from reactions followed in the observation chamber were subsequently collected in aqueous ammonium chloride by means of the exit port. The organic materials were separated and analyzed by gas chromatography. The products were dihydronaphthalene and naphthalene identical with the products obtained under preparative scale conditions. We can conclude that the reaction studied at low concentrations is the same as that observed at higher concentrations.

Isotope Studies. The kinetic isotope effect was determined using THF solutions of deuterium oxide (D_2O). Table IV records the results. Although the per cent error is substantial, there is no doubt that the isotope effect is small. We interpret this result as consistent with the transition state depicted for the reaction by Streitwieser.[21] He assumes that the transition state for protonation of radical anions involves only a perturbation of the original π-electron system, and transition state thus resembles starting material with little bond formation. Under these conditions little discrimination for O–H or O–D is expected since bond breaking occurs after the transition state.

Table IV. Rate Constants and Kinetic Isotope Effects for the Reaction of Sodium Naphthalene with Deuterated Water

Temp, °C	$k^a \times 10^{-3}$	k_H/k_D
10	2.80 ± 0.56	1.89
15	7.70 ± 0.56	0.96
20	7.94 ± 0.98	1.27
		Av 1.37 ± 0.44

[a] For sodium naphthalene in tetrahydrofuran with concentrations of 0.37–$1.95 \times 10^{-4}\ M$.

The products of this reaction were collected by gas chromatographic trapping techniques and analyzed by mass spectral analysis. Table V records the results. Focusing attention first on the peaks at 130 and 132, these correspond to dihydronaphthalene and its deuterated analog, respectively. The dihydronaphthalene arises from protonation of radical anion before reaction in the observation chamber. In control experiments (see Experimental Section) we have established that of

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[14] Estimated from model compounds found in E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 27, and references therein.

[15] C. A. Coulson and A. Streitwieser, "Dictionary of π Electron Calculations," W. H. Freeman, New York, N. Y., 1965.

[16] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 343.

[17] J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

[18] C. D. Ritchie, *ibid.*, **91**, 6749 (1969).

[19] W. D. Closson and S. Bank, unpublished data.

[20] S. Bank and D. A. Noyd, *Tetrahedron Lett.*, 1413 (1969).

[21] (a) A. Streitwieser, AFOSR Report No. 547, March 1961; (b) U. S. Dept. Com. Office Tech. AD 255, 313 (1961).

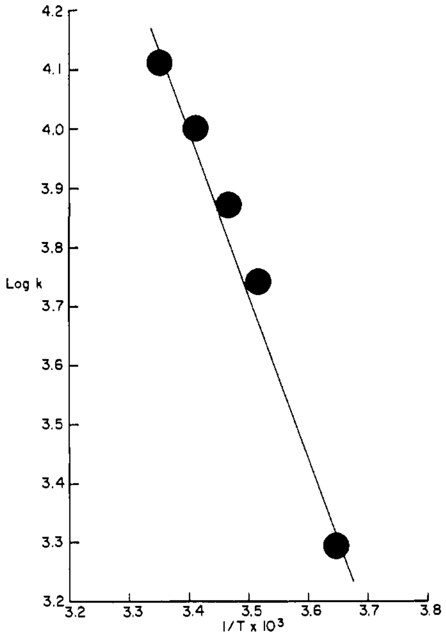


Figure 2. Arrhenius plot for the reaction of sodium naphthalene with water in THF over the temperature range 1–25°.

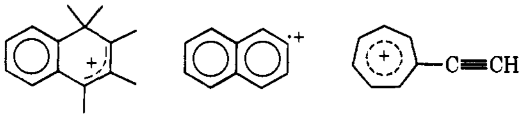
the total protonation products approximately 80% of them occur before reaction in the chamber. This is confirmed by the mass spectral data which give 12.4% dideuterio product.

Table V. Mass Spectrum[a] of Products of Sodium Naphthalene and Deuterium Oxide Reaction

Mass/charge	Relative abundance[b]
128	100
129	32.8
130	14.4
131	3.5
132	2.0

[a] Obtained at 10 eV. [b] Corrected for ^{13}C in natural abundance

Calculation of the per cent dideuterio product was made after correction for the fragmentation pattern of pure dihydronaphthalene. The mass spectra of pure dihydronaphthalene was recorded under the identical conditions. The *m/e* peaks and relative intensities are 131 (1.2), 130 (100), 129 (21.0), 128 (15.7), 127 (0.3), and 115 (6.9). In addition to the molecular ion, major peaks result from loss of H (*m/e* 129), H_2 (*m/e* 128) and CH_3 (*m/e* 115). The resonance stabilized species that could reasonably be involved are



A small metastable peak at 101.8 links the 115 fragment with the molecular ion.

The per cent dideuterio product was 12.4%, as found by properly weighting the molecular ion peaks. This is close to the expected value based on the amount of radical anion consumed in the observation chamber.

Table VI. Second-Order Rate Constants for the Reaction of Sodium Naphthalene as a Function of Temperature

Temp, °C	$k \times 10^4$, M^{-1} sec^{-1}
25.0	1.35 ± 0.31
20.0	1.01 ± 0.18
15.0	0.74 ± 0.53
11.0	0.55 ± 0.50
1.0	0.20 ± 0.06

Activation Parameters. Table VI records the rate of reaction as a function of temperature and Figure 2 depicts the activation plot. From the slope a value of $E_a = 10.6 \pm 2.0$ kcal/mol is obtained. The values of the enthalpy and entropy of activation are $\Delta H^{\ddagger} = 10.0 \pm 1.9$ kcal/mol and $\Delta S^{\ddagger} = -6.2 \pm 2.5$ eu, respectively. These results are also in marked agreement with the Streitwieser depiction of the transition state. Whereas full protonation of the radical anion involves the loss of some 60 kcal/mol resonance energy, the small observed activation energy indicates that transition state occurs very early with only a small fraction of this loss.

Finally, the activation energy may be compared with the value obtained in the radiolysis studies. For naphthalene in isopropyl alcohol the value is 3.4 kcal/mol.[8b] The activation parameters indicate that the two systems are markedly different, and the similar values for the rate constants are accidental. This is not surprising in view of the vast differences in the two systems, of which the most significant differences that render any strict comparison meaningless are the counterion and solvent. The nature of the two counterions and their disposition with regard to the anion in the two systems are diametrically opposite. Furthermore, the solvent effect in mixed solvent systems is of commanding importance,[22] and extrapolation of results obtained in pure solvents to the mixed system is meaningless at this time.

The State of Ionic Aggregation and Reactivity. The importance of solvation in radical anion chemistry has been emphasized in many studies. For leading references, see the work by Szwarc.[23] The important role of solvation can be underlined by briefly reviewing a few points. Many studies emphasize the importance of etheral solvents to the stability of radical anions. For the equilibria, K may vary greatly depending on the choice of ether.[24a] Steric effects are more important

$$\mathrm{Ar} + \mathrm{Na\ (metal)} \overset{K}{\rightleftharpoons} \mathrm{Na^+Ar\cdot^-}$$

than bulk polarity, indicating that a specific coordination of solvent with cation is involved.

The effect of ionic aggregation on the physical properties of aromatic radical anions has been long known,[24b] and has received considerable attention.[8c,24c] Understanding the variation of these properties has been possible with the concept of thermodynamically distinct ion pairs in dynamic equilibria.[27] For a number of systems, the different ion pairs involved have been iden-

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(22) L. Dorfman, private communication.

(23) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., 1968.

(24) (a) R. V. States and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 6043 (1967); (b) G. J. Hoijtink, E. deBoer, P. H. van der Meij, and W. P. Wiejland, *Recl. Trav. Chim. Pays-Bas*, **74**, 277 (1955); (c) E. deBoer, *Advan. Organometal. Chem.*, **2**, 115 (1964); (d) T. L. Chu and S. C. Yu, *J. Amer. Chem. Soc.*, **76**, 3367 (1954).

tified, and the relevant thermodynamic parameters, K, ΔG, ΔH, and ΔS have been determined for the respective equilibria. Uv-visible spectroscopy, conductimetry, and esr techniques have all been employed to distinguish among the ion pairs and to determine the equilibrium constants.[6,27,28] For instance, naphthalene radical anion pairing phenomena have been studied as a function of counterion, solvent, and temperature.[6,25] In addition, it has been established by magnetic susceptibility studies that sodium naphthalene is monomeric in THF solution.[24d] Therefore, aggregation beyond ion pairs is not important. These important data have helped to provide a more quantitative understanding of the specific solvation of counterion in etheral solvents. In addition, the state of ionic aggregation greatly affects the physical properties of aromatic radical anions.

Chemical reactivity is also a function of the state of ion aggregation. Hirota has examined in detail the electron exchange reaction between $Na^+Nap\cdot^- +$ Nap.[26a] They found that the rate of electron transfer varies over a range of nearly two orders of magnitude. All of these reactions are fast, with rate constants typically about $10^8\ M^{-1}\ sec^{-1}$. The activation energies varied monotonically with the state of ion pairing. The values are 2.5, 3.1, and 4.6 kcal/mol for the free, loose, and contact ion pairs in THF or THF–DME solvent mixtures, respectively. While free ions react at close to diffusion-controlled rates, contact ion pairs are considerably slower. As Weissman pointed out,[26c] this is not unexpected since transfer between free ions is formally a simple electron transfer, while transfer between ion pairs is a formal atom transfer. Therefore, these results are a direct consequence of the state of ionic aggregation.

One striking phenomenon, an apparent "negative" activation energy, was exposed by a temperature study of the kinetics of electron exchange between $Na^+Nap\cdot^-$ + Nap in THF.[26a,b] The Arrhenius plot shows an anomalous positive slope in the temperature range −30 to 30°. The explanation depends on a consideration of the equilibria of loose and tight ion pairs. Low temperature favors the loose ion pairs, and through the critical temperature range a population inversion occurs. The more reactive loose pairs increase from a small minority to a predominant majority, producing a concommitant increase in the exchange rate. Separately, they demonstrated that the temperature behavior of the rate constant for each ion pair is normal. Since the temperature variation of the relevant equilibrium constant is known, anamolous behavior can be expected for those cases where loose ion pairs are more reactive than tight ion pairs. Therefore, when a population inversion is known to take place, a "negative"activation energy is a diagnostic for greater reactivity of the predominant low-temperature species.

We addressed attention to the question of how the state of ion pairing effects the nucleophilic reactivity of aromatic radical anions. For this purpose, the rates of proton abstraction from water were measured for sodium naphthalene in several states of aggregation. These were chosen to provide systems where the known equilibrium constant favored one ionic form greatly over the others.[1,6c,27] Thus the order of reactivity can be established for the series of isomeric ion pairs. Before an interpretation of the data in terms of a reactivity series can be made, there must be an assurance that the rate constants determined can be confidently assigned to their respective ion pairs. Three possibilities exist that could cast the assignments in doubt. If the proton abstraction rate constant for any one of the three ion pairs was greater than its rate of appearance in the ion pair equilibria, the measured rate constant would reflect the latter rather than the former rate. Consider the equilibria

$$\underset{\text{tight}}{Na^+Nap\cdot^-} \overset{K}{\rightleftharpoons} \underset{\text{loose}}{Na^+||Nap\cdot^-} \overset{K}{\rightleftharpoons} \underset{\text{free}}{Na^+\ Nap\cdot^-} \qquad (22)$$

Any one of the three could be a candidate for a highly reactive species. The rate-determining step would then become the association or dissociation that produced the reactive species, rather than the proton abstraction step. However, these three possibilities may be excluded for the following reasons. . First, with regard to tight ion pairs, esr studies have shown that the rate of collapse to tight ion pairs is rapid. For example, the rate constants for collapse from loose to tight ion pairs in THF–DEE at −70° is $1.5 \times 10^7\ sec^{-1}$.[26a] Further, the lifetime of a glymated ion pair in THF at 25° is estimated as 10^{-6} sec.[6c] As the half-lives of these interconversions are orders of magnitude smaller than that observed for proton abstraction, collapse of ion pairs cannot be rate determining. Second, since the system of predominantly loose ion pairs provides the smallest rate constant, this species cannot be highly reactive. Finally, with regard to free ions, those systems expected to be more favorable for the formation of free ions (DME–THF and THF–tetraglyme) also have the smaller rate constants, again contrary to a dissociation mechanism. Having now excluded these possible complications, the assignments of the observed rate constants to the proton abstraction step by the predominating ion pair can be made confidently.

Table VII summarizes the data obtained for four different ion pair systems. Good pseudo-first-order behavior was observed in all of the systems studied, except for the tetraglymated ions. The rate plots had a definite curvature for $[H_2O] = 9.1 \times 10^{-3}\ M$; the initial slope was about twice the final slope. However, at $[H_2O] = 0.066\ M$, good pseudo-first-order kinetics were obtained with a rate constant that agreed with the slow portion of the lower $[H_2O]$ runs. Noting this agreement, we postulate that certain changes of solvation occur due to the accumulation of base during the course of reaction. These changes must be similar to those induced by addition of the larger excess of water, and may have subtle effects on the ion pairs that do not easily lend themselves to explanation by kinetic experiments. However, this complication does not alter the conclusion that the glymated pairs are substantially less reactive than the tight ion pairs.

Inspection of Table VII provides a number of interesting facts. First, although the general range of reactivity must be classified as only moderately fast, the individual rate constants vary by a factor of approximately

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(25) N. Hirota, *J. Amer. Chem. Soc.*, **90**, 3603 (1968).

(26) (a) N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90**, 3611 (1968); (b) P. J. Zandstra and S. I. Weissman, *ibid.*, **84**, 4408 (1962); (c) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958).

(27) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, 70, 3180 (1966).

Table VII. Rate Constants and Derived Data for the Reaction of Sodium Naphthalene and Water in Various Solvent Systems

System	Ion pair	$k^{20°}$ ($\times 10^{-4}$)	ΔE_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
THF	Tight	1.06	10.6 ± 1.9	10.0 ± 1.9	−6.2 ± 2.5
THF/DME[a]	Loose and free	0.78_6	14.1 ± 4.0	13.5 ± 3.8	+5.3 ± 10
DME	Loose	0.31	13.6 ± 3.4	13.0 ± 3.2	+13.2 ± 11
THF/tetraglyme[b]	Glymated	0.023_4[c] 0.042_8[d]	17.7 ± 5.0	17.3 ± 4.8	+22.5 ± 16.4

[a] 50/50 by volume mixture achieved by mixing $Na^+Nap\cdot^-$ in THF with H_2O in DME. [b] 100/1 molar ratio of (tetraglyme) to ($Na^+Nap\cdot^-$) For

$$Na^+Nap\cdot^- + g \overset{K}{\rightleftharpoons} Na^+Nap\cdot^-g$$

K = 200–300 M^{-1}.[6c] [c] $[H_2O]$ = 0.066 M. [d] $[H_2O] = 9.1 \times 10^{-3}$ M.

50. There is a monotomic decrease in reactivity from tight to glymated ion pairs, and therefore, the proton abstraction reaction is not only slower than the electron-transfer reaction, it also has a reactivity series of substantially different order. Second, the activation parameters parallel this trend. In fact, the $\Delta H^{\ddagger}$ term varies to a greater extent than would be apparent from a simple comparison of the rate constants, because the variation of $\Delta H^{\ddagger}$ is partially offset by an opposing variation in $\Delta S^{\ddagger}$. Finally, all the Arrhenius plots behave in a normal manner. It is useful to apply the diagnostic derived from the electron-transfer studies. Contrary to what is found in electron transfer studies at these temperatures in THF or THF–DME systems, the Arrhenius plots have negative slopes, which confirms that loose ion pairs are less reactive than tight ion pairs. In THF at 25° approximately 7% of sodium naphthalene is in the form of loose ion pairs; at 0° approximately 15%,[26a] and, therefore, the measured activation energy may be somewhat higher than the "true" value for "pure" tight ion pairs in THF. Correspondingly, $\Delta S^{\ddagger}$ for "pure" tight ion pairs would be somewhat less than −6.2 eu. In sum, these three facts indicate that the trend in nucleophilic reactivity is directly opposite to the trends found for electron-transfer reactions.

To account for this contrary behavior, examination of the factors involved in the electron-transfer reaction is profitable because solvation factors exert an influence in both types of reactions. In the electron-transfer reactivity series, the free ion exchanges the fastest, the tight ion pairs slowest. This reflects the difference between an electron transfer and an atom transfer. Free anions are not extensively solvated and little solvent reorganization is expected in the transition state.[27] These reactions are near the diffusion control limit. During the atom transfer process, solvent molecules must be removed from the ion pair solvation shell and reorganized to produce a transition state with the positive counterion symmetrically shared by two organic molecules.[26a] This reorganization costs energy which is reflected in a higher ΔE_a. Szwarc, *et al.*,[6c] has found two forms of glymated ion pairs, one of which also has a nearly diffusion-controlled rate of exchange. They propose a solvent–ion pair structure that can easily form a symmetrical transition state of two aromatic molecules sharing a counterion. A second glymated ion pair unable to form this intermediate without solvent reorganization has a slower exchange rate. The height of the barrier is thus critically dependent on the extent of solvent reorganization in the transition state. As the reactant and product are isoenthalpic, the state of ion pairing can neither raise nor lower the ground state with respect to product. This is not true with the proton abstraction reaction, so it is therefore not surprising that the orders of reactivity are different. In proton abstraction there is an additional factor, the comparative ground-state energies of the ion pairs, that is mutually cancelled in the "invisible" reaction of electron exchange.

Contrasting our results with those obtained in a study of the protonation of delocalized carbanions is informative. Hogen-Esch and Smid studied the effect of ion pairing on the reactivity of fluorenyl carbanions.[9c,28] The proton source was either 1-, 2-, or 3,4-benzofluorene, and solvent systems produced either contact, solvent-separated, or glymated ion pairs. In these systems, solvent-separated ion pairs in DME are more reactive by a factor of 25–100 than contact ion pairs in either DME or THF. Less energy is required to transfer the counterion to the new carbanion if the pairs are solvent separated. However, the salts of larger alkali metal cations are somewhat less reactive than is the sodium salt, contrary to a prediction based on ease of counterion transfer. The authors deduce a catalytic activating role for the counterion, as sodium should be more effective in this role. Glymated fluorenylsodium is also less reactive than is expected for a solvent-separated pair. In this case the steric bulk of tetraglyme inhibits the approach of the aromatic proton donor. In summary, three effects control the reactivity of the fluorenyl ion pairs investigated, an energy of transfer for the counterion, a catalytic role for the counterion which increases with decreasing ionic radii, and a steric effect which is pronounced for tetraglyme, but of much less importance for DME. Solvent-separated fluorenylsodium ion pairs in DME, the most reactive carbanion, is the most favorable blend of these three parameters.

In contrast to the benzofluorene–fluorenyl anion system, the reactivity of $Nap\cdot^-Na^+$ ion pairs toward water seems to be governed by somewhat different factors. Note that both loose and glymated ion pairs are less reactive than tight ion pairs. To explain this the steric arguments used above can hardly be invoked when water is the proton donor. The sodium naphthalene case cannot be understood by drawing simple analogies from either the electron transfer or the carbanion work.

Two alternative hypotheses are attractive. First, a catalytic role for the counterion may dominate all other factors. The spatial arrangement of radical anion, counterion, and water must then be most favorable in the tight ion pair. The effect is inhibited somewhat in the loose ion pair and more so on glymation. The trend in activation parameters shows that the more the effective catalysis is in lowering $\Delta H^{\ddagger}$, the more order is

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(28) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **89**, 307 (1966).

required in the transition state. By this hypothesis, reactivity is governed by the counterions' ability to ease H–OH bond breaking.

In the second hypothesis we focus attention on solvation of the cation. Consider the enthalpy and entropy changes associated with the formation of loose ion pairs and free ions from tight ion pairs in THF There is a favorable enthalpy change of -5.6 and -3.7 kcal/mol in successive steps, and an unfavorable entropy change of -24 and -38 eu due to the concommitant order induced in the solvent.[26a] In the proton abstraction reaction, it is reasonable to expect solvent–cation interaction will contribute to lowering $\Delta H^{\neq}$ in proportion to the enthalpy gains possible by dissociation to free ions in that solvent system. Thus, this advantage is greatest for tight ion pairs in THF, $\Delta H_{\text{diss}}{}^0 = -9.2$ kcal, and least for glymated ion pairs, $\Delta H_{\text{diss}}{}^0 = 0$ in THF.[6c] If this effect is larger than any changes induced by bulk solvent properties, there are grounds for considering the tight ion pair in THF as a ground state of higher energy that its "isomers" in other solvents. This is a large assumption, but this effect may be especially important in this system because the reaction is quite exothermic, the transition state comes early—both of which make the activation barrier more sensitive to changes in ground-state energy, and the product, OH^-, is a small, hard base rather than a delocalized carbanion. Its solvation energy is likely to vary less with solvent, again reducing the cancellation of effects noted particularly in electron-transfer reactions. The higher reactivity of the tight ion pair can thus be rationalized by the greater advantage gained by increased cation solvation in the transition state. It is reasonable that this enthalpy gain would be partly compensated by a more negative $\Delta S^{\neq}$ term, which is consistent with the data. It is also interesting to note that the transition state for loose ion pair formation lies very near the tight ion pair.[26a] Thus both the proton abstraction and cation solvation reactions have early transition states. It is plausible that a parallel exists between the proton abstraction step and the cation solvation step. This hypothesis is distinct from the first because the counterion is not required to interact with the same water molecule donating its proton. More complicated pictures than just the four-centered stretch of the H–OH bond of the catalysis hypothesis can be imagined. Work in progress may establish which hypothesis is more nearly true.

In summary, this kinetic study indicates that the proton transfer from water is many orders of magnitude slower than typical electron transfer reactions, and that both of these reactions may be controlled to some degree by the state of ion pairing. When the reduction potentials of sodium naphthalene and an oxidizing agent are favorable for fast electron transfer, this transfer should be competitive even though water may be in large excess. Also the course of reaction may be controlled in situations where sodium naphthalene partitions between nucleophilic and electron transfer pathways. Tight ion pair systems may favor the nucleophilic pathway while glymated ion pairs may favor the electron transfer pathway. These considerations may make sodium naphthalene a more versatile reagent than is now realized. For example, could naphthalene be used as a catalytic electron transfer agent for reductions in the presence of protic solvents? Is there a way of further extending our limits of control over these reactions? These questions are being actively pursued.

Experimental Section

Materials. Naphthalene was obtained from Eastman Organic Chemicals no. 168 or Matheson Coleman and Bell No. NX5, and used without further purification. Deuterium oxide (99.8% D) was obtained from Stohler Isotope Chemicals. THF, chromatoquality from Matheson Coleman and Bell, and DME Puriss grade from Aldrich Chemical Co. were both distilled from benzophenone sodium ketyl just prior to use. Tetragylme, from Eastman Organic Chemicals, was vacuum distilled from Na–K alloy, then redistilled from benzophenone sodium ketyl prior to use, bp 128° (7 mm).

Preparation of Radical Anion. A flask similar to the design of Waack and Doran was used for the preparation of radical anion solutions.[12] Solvent was distilled onto freshly cut metallic sodium and a glass-covered magnetic stirring bar. At the end of distillation, the flask was removed from the still, a weighed amount of naphthalene added, and the flask quickly stoppered. The radical anion color was generated within hours; solutions were stirred at least 1 day before use. The visible spectrum was recorded with a Cary 14 spectrophotometer after filling a 0.0139-cm cell attached to the side arm. Spectra obtained agree with the published spectra.[11] Solutions were transferred to the stopped flow device by gas tight syringes.

Stopped-Flow Apparatus. The basic design is that of Gibson and Milnes, with modifications by Ritchie.[10,29] Our machine uses stainless steel drive syringes rather than the fragile glass variety. To accomodate the reactivity of radical anion solutions, all parts were made of stainless steel, glass, or nylon. The sole exception is the drive syringe tips, where the properties of Teflon are required to give a durable, gas-tight seal. A visible reaction takes place at these tips, consuming considerable amounts of radical anion. The general procedure to overcome this effect is to prepare a stock solution of $\sim$1–2 $\times 10^{-2}$ *M* $Na^+Nap\cdot^-$. After transfer and 10–15 min thermal equilibration, the estimated concentration within the machine is $\sim 5 \times 10^{-4}$ *M*. At the point of initial observation, the concentration is typically about 1×10^{-4} *M*. The exact concentration is determined by the absorbance.

Ancilliary equipment for the apparatus includes a Baush and Lomb high-intensity grating monochromator No. 33-86-25-02, for the visible range, with 25-V G.E. 1958 tungsten–iodide lamp to replace the smaller lamp supplied with the instrument. The lamp power supply is two surplus 12-V Zener diode regulated IBM supplies in series. Output of the photomultiplier (RCA 1P28), operated with a Beckman DU power supply (No. 73602), is fed directly to a storage oscilloscope (Tektronics type 564B with plug-ins type 2A63 differential amplifier and 2B67 time base). Polaroid photographs may then record the event at the operators convenience. The entire mixing apparatus is enclosed in a thermostat maintained by a constant-temperature bath. The observation chamber is of 2 mm bore, 20 mm long, and sealed at both ends with quartz windows and nylon washers. A manual push of the drive syringe is sufficient for our purposes. The half-life of a fast reaction at typical conditions is $\sim$10 msec.

The performance of the apparatus was evaluated by measurement of the rate constant of dehydration of carbonic acid. Our value, $k_1 = 24.5 \pm 1.8$ sec^{-1}, agrees with Dalziel's data extrapolated to 25.0°.[30]

$$H_2CO_3 \xrightarrow{k_1} H_2O + CO_2$$

Water Determinations. The water concentration of stock solutions was determined by Karl Fischer titration with a Labindustries aquametry apparatus.

Product Analysis. The reaction products were analyzed by glpc using a 4-ft Carbowax column at 160°. Dihydronaphthalene and naphthalene were identified by comparison of retention times with the authentic material. Mass spectra were recorded on a AEI-MS 902 high-resolution mass spectrometer.

Acknowledgment. We acknowledge with gratitude support of this work by The National Science Foundation. We are grateful for the expert help of Mr. Charles Houghton in the construction of the rapid mixing apparatus.

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(30) K. Dalziel, *ibid.*, **55**, 79 (1953).