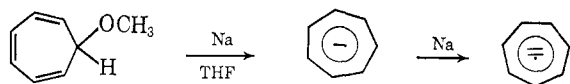


Figure 1.

min.), while periodically removing samples for e.s.r., gives a deep green radical. The e.s.r. spectrum (Figures 2 and 3), recorded at  $-100^\circ$ , is an octet (splitting



by seven equivalent protons with hyperfine splitting constant  $a_H = 3.48$  gauss). Each member of the octet is further split into a septet ( $a_{2Na^+} = 1.74$  gauss) which is best seen by magnifying the wings of the spectrum.

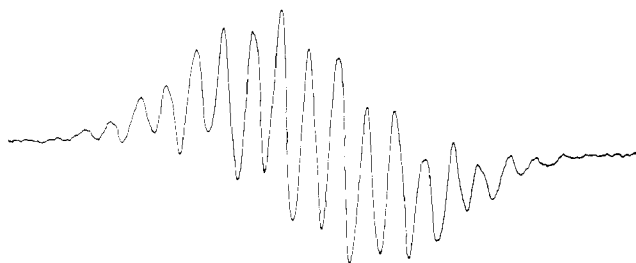


Figure 2. E.s.r. spectrum of disodium tropenide in THF at  $-100^\circ$ .

$^{23}\text{Na}$  has nuclear spin  $I = 3/2$ . Two sodium nuclei thus have an aggregate nuclear spin of  $I = 3$  and lead to  $2I + 1 = 7$  lines. No previous instance of splitting by two alkali metal ions has ever been noted for hydrocarbon radicals.<sup>4</sup> This is seen as compelling evidence that the observed radical is a dianion. The major splitting by seven equivalent protons excludes all possibilities other than the cycloheptatrienide (tropenide) dianion radical.<sup>5</sup>

The value of  $a_H$  calculated from the simple McConnell equation<sup>7</sup> is  $a = -3.86$  gauss. Employing the

(4) Splitting by one metal nucleus is common among anion radicals. See, e.g., the  $a_{Na^+} = 1.05$  gauss shown by sodium naphthalene in THF: N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961). We also have noted splitting by two metal ions in other dianion radical e.s.r. spectra.

(5) J. Dos Santos-Veiga, *Mol. Phys.*, **5**, 639 (1962), has observed an eight-line spectrum, not further resolved, upon reaction of ditropyl with potassium-sodium alloy in DME. This was attributed to the tropyli radical adsorbed on the metallic surface since decantation or filtration through glass wool greatly weakened the signal. This interpretation is invalidated by the following observations: (i) the initially formed blue species (tropenide anion) is diamagnetic and only later is the green radical formed; (ii) the radical is stable after decantation from the metal even after several hours; (iii) the tropyli radical has  $a = -3.87$  gauss or greater at  $-100^\circ$ ; (iv) filtration, *in vacuo*, through a fritted glass filter does not reduce the intensity or resolution of our signal; and (v) the signal is split by two alkali metal ions.

(6) G. Vincow, *Chem. Eng. News*, **43**, No. 26, 43 (1965).

(7)  $a_{Hi} = Q\rho_i$  where  $Q = -27$  gauss and  $\rho_i$  is the spin density at carbon  $i$  (here  $1/7$ ): H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

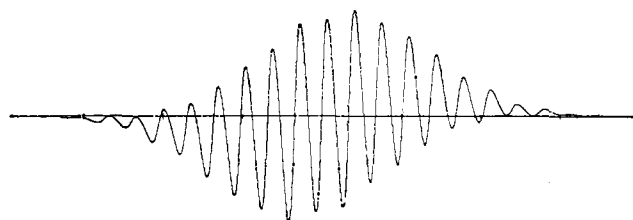


Figure 3. Calculated spectrum of disodium tropenide.

Colpa-Bolton equation<sup>8</sup>  $a_H = -3.34$  gauss is predicted. The experimental value is in much better accord with the latter equation, which predicts lower h.f.s. for more negatively charged radicals. No doubt part of the small disagreement stems from the temperature dependence of the h.f.s.<sup>6</sup>

The cycloheptatrienide dianion radical should be subject to Jahn-Teller stabilization, but no evidence is available on this point.

**Acknowledgments.** We thank the National Institutes of Health for support of this research and Messrs. Larry Wheeler and Tom Atkinson for e.s.r. measurements.

(8)  $a_{Hi} = Q_1\rho_i + Q_2q_i\rho_i$ , where  $q_i$  is the charge density at carbon  $i$  ( $-2/7$  here).  $Q_1$  and  $Q_2$  are taken as  $-27.0$  and  $-12.8$  gauss<sup>9</sup>: J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(9) L. Snyder and T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).

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## Catalysis of Phosphoryl Group Transfer by Alkali Ions

Sir:

Specific catalysis by alkali ions is not a common occurrence in chemistry and therefore may be of considerable interest, particularly to investigators concerned with the transport of sodium and potassium ions through biological membranes. Verheyden and co-workers<sup>1</sup> reported that in the absence of pyridine nucleoside polyphosphates do not dismutate in dimethyl sulfoxide solutions of their tri-*n*-butylamine salts. We found likewise that there was no appreciable phosphoryl group transfer between adenosine 5'-diphosphate (ADP) molecules in a dimethyl sulfoxide solution of their tetra-*n*-butylammonium salt at 25 and 60 $^\circ$ , respectively. However, partial or complete replacement of the tetra-*n*-butylammonium ion by  $\text{Na}^+$  or  $\text{K}^+$  causes the phosphoryl group transfer to take place readily at these temperatures.  $\text{Rb}^+$  and  $\text{Cs}^+$  also catalyze this reaction, but  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Zn}^{2+}$  do not.

In the present work the ADP was used in the form of the tri- or bis(tetra-*n*-butylammonium) salt, prepared by stirring stoichiometric amounts of the barium salt of ADP (Sigma Chemical Co.) and tetra-*n*-butylammonium sulfate, centrifuging out the precipitated  $\text{BaSO}_4$ , and freeze-drying the supernatant. The early phase of the dismutation reaction of ADP in dimethyl sulfoxide (DMSO, Matheson, Spectral Quality) solution was followed by measuring the rate of increase of ATP

(1) D. L. M. Verheyden, W. E. Wehrli, and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 2257 (1965).

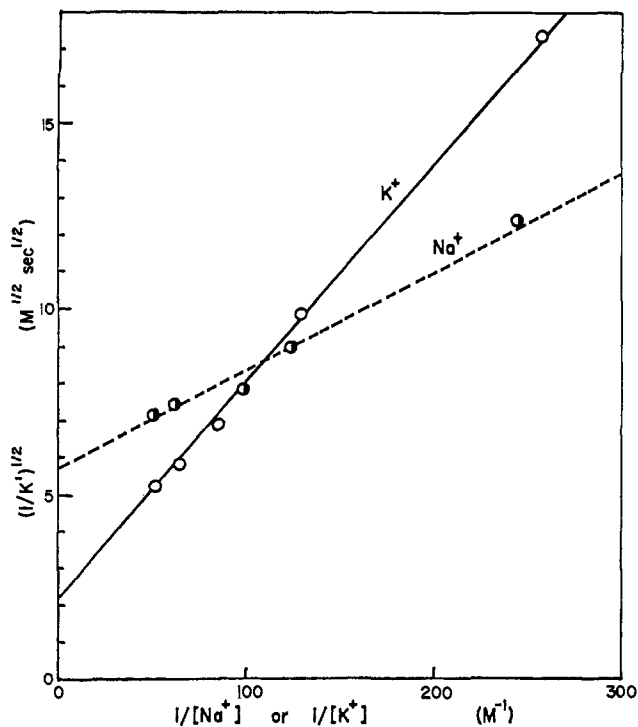


Figure 1. Dependence of the apparent second-order rate constant on sodium or potassium ion concentration.

concentration. The ATP formed was assayed by means of the fluorometric method described by Esterbrook.<sup>2</sup> A Farrand A2 fluorometer was used with Siliclad glass sample cells.

At constant concentration of Na<sup>+</sup> or K<sup>+</sup>, it was found that the initial rate of phosphoryl group transfer according to the equation  $2\text{ADP} \rightleftharpoons \text{ATP} + \text{AMP}$  is proportional to the square of the ADP concentration. However, the apparent second-order rate constant,  $k'$ , varies with the nature and concentration of the alkali ion in a way which can be quantitatively accounted for by assuming that the rate-determining step involves the reaction between two ADP-Na<sup>+</sup> or ADP-K<sup>+</sup> complex ions. For example, if we define the apparent stability constant,  $K'$ , of the ADP-Na<sup>+</sup> complex as

$$K' = \frac{[\text{ADP-Na}^+]}{[\text{ADP}][\text{Na}^+]} \quad (1)$$

then the initial rate of dismutation may be written as

$$\frac{1}{2} \frac{d[\text{ATP}]}{dt} = k'[\text{total ADP}]^2 = k[\text{ADP-Na}^+]^2$$

Hence we have

$$\left(\frac{1}{k'}\right)^{1/2} = \left(\frac{1}{k}\right)^{1/2} \left(1 + \frac{1}{K'[\text{Na}^+]}\right) \quad (2)$$

where  $k$  is the true second-order rate constant.

In Figure 1 the values of  $(1/k')^{1/2}$ , where  $k'$  is the measured apparent second-order rate constant, are plotted vs. the reciprocal of alkali ion concentration. For these measurements solutions of the bis(tetra-*n*-butylammonium) salt of ADP in DMSO solution at 60° were used. The initial concentration of total ADP was in the range  $5.9$  to  $6.6 \times 10^{-4} M$ . The Na<sup>+</sup> or K<sup>+</sup>

(2) R. W. Esterbrook, *Anal. Biochem.*, **4**, 231 (1962).

was added in the form of its perchlorate. Enough tetra-*n*-butylammonium bromide was added in each of these solutions to keep the ionic strength constant at  $0.04 M$ . The plots are, within experimental uncertainties, linear as required by eq. 2. The apparent stability constants,  $K'$ , and the true second-order rate constants,  $k$ , are calculated from the slopes and intercepts of these linear plots according to eq. 2 to be  $K' = 37 M^{-1}$ ,  $k = 0.21 M^{-1} \text{sec}^{-1}$  for K<sup>+</sup>;  $K' = 2.1 \times 10^2 M^{-1}$ ,  $k = 0.031 M^{-1} \text{sec}^{-1}$  for Na<sup>+</sup>.

The conclusion that Na<sup>+</sup> and K<sup>+</sup> catalyzed the phosphoryl group transfer through complex formation is further supported by the observation that cations such as Li<sup>+</sup> and Mg<sup>2+</sup> are not only themselves inactive but can also suppress the catalysis by Na<sup>+</sup> or K<sup>+</sup> through competition for the same ligands. The reverse reaction  $\text{ATP} + \text{AMP} \rightarrow 2\text{ADP}$  was also found to be catalyzed by Na<sup>+</sup> or K<sup>+</sup>, although the kinetics are more complex since the ATP molecule may transfer its phosphoryl group either to an AMP molecule or to another ATP molecule.

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(3) Public Health Service predoctoral trainee in biophysical chemistry (5-TIGM-748-05).

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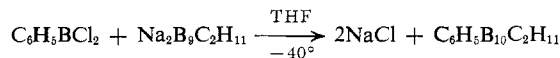
### B-Phenyl-1,2-dicarbaclododecaborane(12) from B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>-2</sup> through an Insertion Reaction

Sir:

We wish to report the first derivative of 1,2-dicarbaclododecaborane(12) which bears an aryl substituent on boron and the novel insertion reaction which led to the formation of this derivative.

Previous work<sup>1-4</sup> established the existence of B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>-2</sup> [(1)-2,3-dicarbollide ion<sup>3</sup>] and its reactions with transition metal derivatives. The latter reactions reconstituted the icosahedron by inserting the metal atom in the open face of the B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>-2</sup> ion. We now report the re-establishment of the 1,2-dicarbaclododecaborane(12) structure by the similar insertion of a boron atom.

Phenylboron dichloride and B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>-2</sup> reacted at -40° in tetrahydrofuran to produce a B-phenyl-1,2-dicarbaclododecaborane(12) (I) which probably bears the phenyl group in the 3-position. I was purified by



sublimation under high vacuum and obtained as a

(1) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(2) M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965).

(3) M. F. Hawthorne and R. L. Pilling, *ibid.*, **87**, 3987 (1965), propose the modified nomenclature system used herein. The nomenclature system as devised for carboranes (R. M. Adams, *Inorg. Chem.*, **2**, 1087 (1963)) does not take into account species such as B<sub>9</sub>C<sub>2</sub>H<sub>12</sub><sup>-</sup>. We suggest that the position of the hole in these species be identified by the number in parentheses preceding the name using the numbering system of Adams.

(4) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Am. Chem. Soc.*, **87**, 3988 (1965).