isopropyl alcohol undergoes a two-electron and glycolic acid a one-electron oxidation. In both the three-

$$(CH_3)_2CHOH + HOCH_2CO_2H + Cr(VI) \rightleftharpoons complex$$

$$complex \xrightarrow[\text{limiting}]{\text{rate}} (CH_3)_2CO + HOCHCO_2H + Cr(III)$$
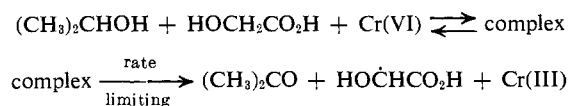
electron oxidation of glycolic acid and in the cooxidation reaction, only carbon–hydrogen bonds are broken. This makes it possible to use deuterium substitution to examine whether the two steps occur simultaneously or consecutively. If the rate-limiting step was a one- or two-electron oxidation leading to a discrete intermediate, then an isotope effect of the same magnitude should be observed for the oxidation of glycolic acid at low and high concentrations and only one of the two substrates in the cooxidation should exhibit an isotope effect; a synchronous mechanism should lead to a substantially large isotope effect at high concentrations of glycolic acid, and to a significant isotope effect for both substrates in the oxidation.

Glycolic-d_2 acid was prepared by LiAlD$_2$ reduction from diethyl oxalate, 2-deuterio-2-propanol from acetone.[3a] The kinetic determination of isotope effects was carried out at three concentrations of glycolic acid: at the lowest concentration the reaction proceeded almost entirely ($>99.4\%$) via the 1:1 glycolic acid–chromic acid complex; at high concentrations of glycolic acid the reaction via the 2:1 complex acquires an increasingly important role. The concentrations of isopropyl alcohol and glycolic acid in the cooxidation ensured that 98% of the observed reaction rate was due to the cooxidation reaction.

The results are summarized in Table I. For the

Table I. Chromic Acid Oxidation of Glycolic Acid and Cooxidation of Isopropyl Alcohol and Glycolic Acid at 25°. Perchloric Acid = 0.628 M

Glycolic acid, M	Isopropyl alcohol, M	10^3k_H, sec^{-1}	10^3k_D, sec^{-1}	k_H/k_D
0.0145		0.0826	0.0134	6.15
3.20		4.20	0.334	12.6
6.01		13.3	0.365	36.5
1.56	0.36	33.0	5.50[a]	5.96[a]
			5.70[b]	5.75[b]
			0.96[a,b]	34.4[a,b]

[a] $(CH_3)_2CDOH$. [b] $HOCD_2CO_2H$.

oxidation of glycolic acid alone, the isotope effect found at high substrate concentrations is very large and totally incompatible with any mechanism in which only a single carbon–hydrogen bond is broken in the rate-limiting step. In the cooxidation reaction both compounds, isopropyl alcohol as well as glycolic acid, exhibit an isotope effect of a magnitude typical for primary kinetic deuterium isotope effects. When both substrates are deuterium labeled an isotope effect of $k_H/k_D = 34.4$ is obtained. This value is almost precisely equal to the product of the separate isotope effect obtained for each of the two substrates.

It is interesting to note that the isotope effect for the one-electron oxidation of glycolic acid, both in the cooxidation and in the oxidation of glycolic acid, is of the same magnitude as the effect for the two-electron oxidations. In this respect, the one-electron oxidation

occurring as part of the three-electron oxidation differs remarkably from the much lower isotope effects ($k_H/k_D = 1.7$–2.4) found for one-electron oxidations by chromium(IV),[7] providing additional evidence that the one-electron oxidation taking place within the termolecular complex is quite different from the oxidation by Cr(IV)$_{aq}$.

The results obtained in this study provide conclusive evidence that *the two bond-breaking processes taking place during the three-electron oxidation occur simultaneously. Consequently, the three-electron oxidation itself proceeds in a single step without the formation of an even short-lived chromium(IV) or chromium(V) intermediate.* The rate-limiting steps for the two reactions can be represented as follows.

$$HOCHCO_2H + OCHCO_2^- + Cr(III)$$

$$HOCHCO_2^- + (CH_3)_2CO + Cr(III)$$
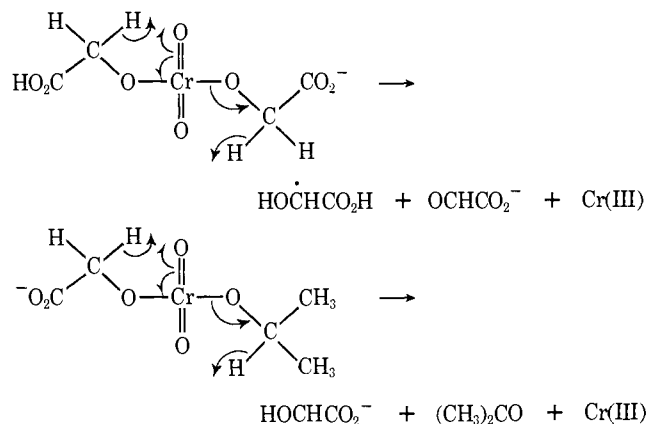
Other transition states involving cyclic complexes between glycolic acid and chromic acid and in which chromium may be octahedral can also be written and should be considered.

(7) J. Roček and C. S. Ng, *J. Amer. Chem. Soc.*, **96**, 1522 (1974).

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Equilibration Studies. Enthalpy Differences between o- and p-Lithioanisoles in Di-n-butyl Ether and Tetramethylethylenediamine

Sir:

Increased understanding of the energies of organometallics will require more thermodynamic information about that class of compounds. However, quantitative thermodynamic data about reactive organometallics has been somewhat difficult to acquire, particularly for the widely used organolithiums and organomagnesiums.[1] We wish to illustrate in this report of the heats

(1) For examples of determinations by different procedures see (a) for heats of combustion and reaction, J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, pp 66–68, pp 444–447; (b) for heats of formation of a number of organomagnesiums, T. Holm, *J. Organometal. Chem.*, **56**, 87 (1973); of ethyllithium and butyllithium, Y. A. Lebedev, E. A. Miroshnichenko, and A. M. Chaken, *Proc. Acad. Sci. USSR, Chem. Sect.*, **145**, 751 (1962); (c) for equilibria in interchanges, D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963), H. J. S. Winkler and H. Winkler, *ibid.*, **88**, 964, 969 (1966); R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *ibid.*, **88**, 460 (1966). (d) for ring-chain equilibria, M. Hanack and H. J. Schneider, *Fortschr. Chem. Forsch.*, **8**, 595 (1967); E. A. Hill, J. Theissen, and K. Taucher, *J. Org. Chem.*, **34**, 3061 (1969); W. C. Kossa, Jr., T. C. Rees, and H. G. Richey, Jr., *Tetrahedron Lett.*, 3455 (1971), A. Mercker and R. Geuss, *Chem. Ber.*, **106**, 773 (1973), and references cited therein.

of conversion of o- and p-lithioanisoles to anisole a straight-forward procedure for determining the relative enthalpies of isomeric organometallics. The present results appear to provide the first quantitative information about stabilization by a substituent bearing non-bonding electrons proximate to the carbon–lithium bond[2] and about the solvent effects of di-n-butyl ether and tertamethylethylenediamine[3,4] on such relative enthalpies.

The isomers o-lithioanisole (1) and p-lithioanisole (2), prepared by metalation of the corresponding bromides with n-butyllithium in pentane under nitrogen,[5] are white, free-flowing powders if protected from the atmosphere. However, in solid form these materials enflame on exposure to air and solutions in di-n-butyl ether (Bu₂O) or tetramethylethylenediamine (TMEDA) were used. The ether solutions were analyzed by Gilman titration[6] and by analytical and preparative glpc of the anisole, anisoles-d_1, and bromoanisoles, which were produced on quenching in separate experiments with water or methanol, deuterium oxide, and ethylene dibromide, respectively. Solutions in tetramethylethylenediamine were analyzed directly by pmr spectroscopy. These experiments established the purity of a number of preparations of 1 as 92–95% active aryllithium with 2–3% residual base and of 2 as 95–99% active aryllithium with 1–5% residual base. The pmr and quench experiments also showed that there is less than 5% interconversion of 1 and 2 in either solution and that quenching with a proton donor gives greater than 95% yields of anisole.[7] Subsequent experiments showed that nontitrable impurities in the samples do not have a significant effect on the values of the heats of hydrolysis (vide infra).

Enthalpies of conversion of 1 and 2 to anisole are provided by the heat evolved when solutions of these compounds are added to absolute ethanol in a calorimeter (Scheme I).[8–10] In each case a graph of calories

Scheme I. Enthalpies of Reaction of o-Lithioanisole (1) and p-Lithioanisole (2) with Ethanol
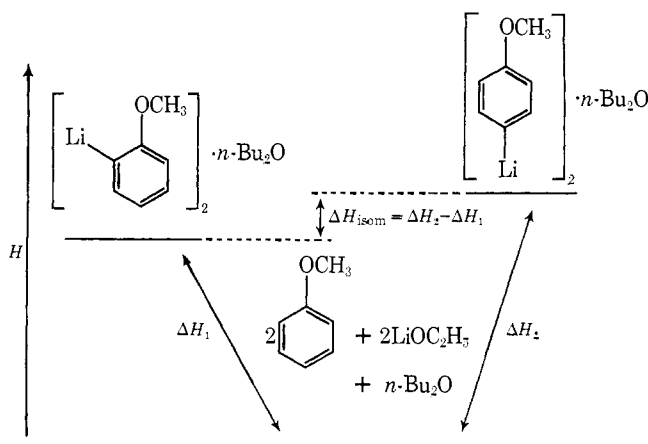
liberated vs. concentration for five to seven points in the range 0.2–0.7 M provides a straight line with a correlation coefficient of 0.9998 or better. The slopes of these lines provide the enthalpies of reaction collected in Table I.[8]

Table I. Heats of Reaction of o-Lithioanisole and p-Lithioanisole in Di-n-butyl Ether (Bu₂O) and Tetramethylethylenediamine (TMEDA) with Ethanol in kcal/mol[a]

| | Solvent | |
Aryllithium	Bu₂O	TMEDA
o-Lithioanisole (1)	−54.5 ± 0.2	−51.2 ± 0.4
p-Lithioanisole (2)	−62.8 ± 0.5	−54.0 ± 0.5

[a] The error limits are standard deviations.

The intercept of the plots was expected and is found to correspond to the heats of solution of di-n-butyl ether and tetramethylethylenediamine in absolute ethanol.[11] The heats of solution of the pure solvents are small relative to the enthalpies of protonation of the aryllithiums, and it would thus be expected that neutral impurities in the aryllithiums would not have a significant effect on the enthalpies of reaction. In fact, a sample which contained 77% 2 and 1% residual base gave an enthalpy of reaction in agreement with that of the purer samples.[12]

Phenyllithium is reported to be dimeric in diethyl ether and tetrahydrofuran between 0.1 and 0.7 M,[13] and this is presumed to be the case for 2 in di-n-butyl ether. We have determined the average association of 1 in di-n-butyl ether also to be predominately dimeric

(2) Enhanced ortho kinetic acidities are attributed at least in part to n-complex formation: (a) D. W. Slocum and D. I. Sugarmen, Advan. Chem. Ser., No. 130, 222 (1974); (b) G. Wittig and G. Fuhrmann, Chem. Ber., 73, 1197 (1940); J. D. Roberts and D. Y. Curtin, J. Amer. Chem. Soc., 68, 1658 (1946); C. D. Broadduss, J. Org. Chem., 35, 10 (1970); R. E. Lundt, G. P. Crowther, and C. R. Hauser, ibid., 35, 1288 (1970); D. W. Slocum and B. P. Koonsvitsky, ibid., 38, 1675 (1973); R. A. Ellison and F. N. Kotsonis, ibid., 38, 4192 (1973), and references cited therein.

(3) For a calorimeteric measurement of the heat of intraction of n-electron donors with two alkyllithiums, see R. P. Quirk, D. E. Kester, and R. D. Delaney, J. Organometal. Chem., 59, 45 (1973); R. P. Quirk and D. E. Kester, ibid., 72, C 23 (1974).

(4) Complexation by TMEDA is kinetically activating: Advan. Chem. Soc., No. 130, (1974).

(5) G. Frankel, S. Dayagi, and S. Kobayashi, J. Phys. Chem., 72, 953 (1968).

(6) H. Gilman and F. K. Cartledge, J. Organometal. Chem., 2, 447 (1964); W. H. Glaze and G. M. Adams, J. Amer. Chem. Soc., 88, 4653 (1966).

(7) The fact that greater than 95% yields of base were produced on quenching with protic solvents provides additional support for the high yields of anisole. The greater than 95% yield of anisole from 2 was determined for a sample which contained 77% 2 and 1% residual base and contained only unreacted p-bromoanisole as the neutral impurity.

(8) The apparatus has been described by P. Beak, T. S. Woods, and D. S. Mueller, Tetrahedron, 28, 5507 (1972), and is based on the work of E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, J. Amer. Chem. Soc., 87, 1541 (1965). P. Beak, D. S. Mueller, and J. Lee, ibid., 96, 3867 (1974), give references to relative enthalpy determinations based on heats of conversion to a common product.

(9) The heat of reaction of n-butyllithium with water has been reported as 57.4 ± 0.7 kcal/mol: P. A. Fowell and C. T. Mortimer, J. Chem. Soc., 3793 (1961).

(10) Heats of deprotonation have been measured for a wide range of Brønsted acids: E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolph, and R. P. Quirk, J. Amer. Chem. Soc., 95, 1492 (1973).

(11) The heat of association of TMEDA with lithium ethoxide is not compensated for by this approach but was determined to contribute less than 1 cal for reactions of 0.7 M 1 and 2 in TMEDA with ethanol which released 54.8 and 57.0 cal.

(12) Three preparations of m-lithioanisole gave material of 76, 87, and 90% purity with about 3% residual base by the Gilman titration. In both solvents the combined data from these samples gave a linear plot for the heats of conversion of active aryllithium to anisole. The values for these heats are 62.2 ± 0.5 kcal/mol in di-n-butyl ether and 54.0 ± 0.7 kcal/mol in tetramethylethylenediamine, within experimental error of those for the para isomer.

(13) D. West and R. Waack, J. Amer. Chem. Soc., 89, 4395 (1967); G. Wittig, F. J. Meyer, and G. Lange, Justus Liebigs Ann. Chem., 571, 167 (1951).

$(+10\%)$ by isopiestic osmometry[14] on 0.56 and 0.71 M solutions.

If differences in kinetic and zero point energies between **1** and **2** are considered to be small, the differences in enthalpies in Table I (ΔH_{isom}) can be taken to reflect differences in chemical binding energies, energies of specific complexation by the solvent and/or more general solvent effects. Differences in heats of solution of the solvents in ethanol have been eliminated by the procedure used to obtain the heats of hydrolysis (*vide supra*). The 8.3 kcal/mol lower enthalpy of **1** with respect to **2** in di-*n*-butyl ether is consistent with intramolecular association of lithium and oxygen[2,3] although for the present case it clearly must be an effect in a dimeric species and a contribution by an inductive effect is possible.[15] It is also consistent with such an effect that this difference is reduced to 2.8 $\pm$ 0.9 kcal/mol in tetramethylethylenediamine a solvent which effectively coordinates with lithium, although the comparison may be tenuous since the state of aggregation of the aryllithiums in TMEDA is not known. The magnitude of differences in specific complexation of isomeric aryllithiums by a common solvent cannot be estimated as yet but it should be noted that total heats of complexation of 2–6 kcal/mol are observed by Quirk for the interaction of different bases with alkyllithiums.[16]

Further speculation about differences in enthalpies will be deferred until more thermodynamic data about isomeric organometallics is available. The present approach should prove exceptionally useful in the acquisition of such information.[17]

(14) The apparatus was constructed by T. L. Brown and colleagues. A MKS Baratron Type 90 is used for the direct measurement of the differential pressure. See J. W. Roddy and C. F. Colman, *J. Inorg. Nucl. Chem.*, **32**, 3891 (1970), for a similar apparatus.

(15) That the contribution of any inductive effect to the enthalpies may be small, is indicated by the lack of a significant difference in the heats of hydrolysis of *m*- and *p*-lithioanisoles.[12]

(16) R. P. Quirk, private communication, Aug 1974.

(17) We are grateful to the National Science Foundation for support of this work, to Professor T. L. Brown for access to the Baratron and to Professor R. P. Quirk for prepublication information.

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A Striking Deuterium Effect in Phosphorus Chemiluminescence. Identification of the Emitting Species

Sir:

Under conditions similar to naturally occurring phosphorus chemiluminescence,[1] a substitution of deuterium oxide for water in the reaction of phosphorus, molecular oxygen, and water was undertaken in our laboratory, and a marked frequency shift and changes in the intensity distribution were observed in the chemiluminescence spectrum. Comparative analysis of the spectra identifies the major emitters in the visible region as $(PO)_2^*$ excimer and HPO. In the ultraviolet we confirm the finding of Rumpf[2] that the major emitting species is PO, and, in the assignment of PO γ (a) and weak PO β bands (b), we also concur with Walsh.[3]

(1) See E. N. Harvey, "A History of Luminescence," The American Philosophical Society, Philadelphia, Pa., 1957.

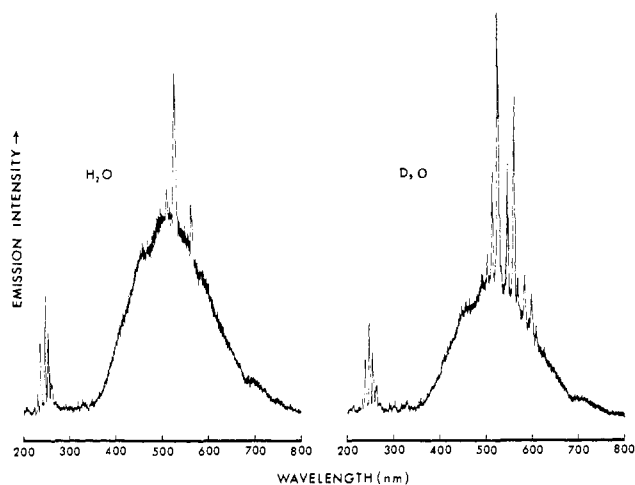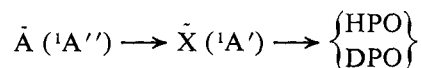(2) K. Rumpf, *Z. Phys. Chem.*, *Abt. B*, **38**, 469 (1938).

Figure 1. Chemiluminescence spectra of phosphorus. Left-hand side chemiluminescence due to the reaction of phosphorus, H_2O, and O_2. Right-hand side chemiluminescence due to the reaction of phosphorus, D_2O, and O_2.

Based on our experiments, our tentative assignments are: (a) 228.8–272.1 nm PO γ system (A $^2\Sigma \rightarrow X^2\Pi$), (b) 325.0–337.0 nm PO β system (B $^2\Sigma \rightarrow X$ $^2\Pi$), (c) 335.0–800 (possibly to 1250) nm; diffuse band system, excimer emission

$$PO^* + PO \rightleftharpoons (PO)_2^* \longrightarrow 2PO + h\nu$$

(d) 450.0–650.0 nm; discrete band system[4-6]

$$\tilde{A} \, (^1A'') \longrightarrow \tilde{X} \, (^1A') \longrightarrow \begin{cases} HPO \\ DPO \end{cases}$$

The phosphorus (Baker) source was a 50-ml glass flask immersed in a water bath (57°). Nitrogen (Airco) saturated with H_2O or D_2O (Columbia, 99.5%) at room temperature was passed through a flask into a 3-mm glass tube. Chemiluminescence occurred at the end of the tube, with air being used as the source of molecular oxygen. A 0.3-m McPherson Model 218 monochromator with an EMI 9558 QB photomultiplier, an Eldorado Model 201 universal photometer, and a Sargent Model TR recorder were used to obtain the spectra.

In Figure 1 the continuum which produces most of the visible green color starts at around 335.0 nm and extends to 800 nm. (In a different experiment performed only with H_2O and using a RCA 7102 photomultiplier and a Warner Swasey scanning monochromator coupled to a Nicolet 1074 signal averager, the continuum extends to 1250.0 nm). We are tentatively suggesting that this emission originates from $(PO)_2^*$ excimer,[7] based on the following considerations. (1) The Walsh[3] excitation mechanism proposed to explain the PO β and γ band emission is

$$P(^4S) + O (^3P) + PO (X \, ^2\Pi) = PO (X \, ^2\Pi) + PO (A \, ^2\Sigma^+ \text{ or } B \, ^2\Pi)$$
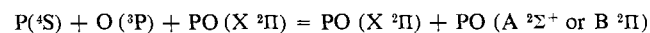
(3) A. D. Walsh in "The Threshold of Space," M. Zelikoff, Ed., Pergamon Press, London, 1957, p 165.

(4) M. Lam Thanh and M. Peyron, *J. Chim. Phys. Physicochim. Biol.*, **60**, 1289 (1963).

(5) M. Lam Thanh and M. Peyron, *J. Chim. Phys. Physicochim. Biol.*, **63**, 266 (1966).

(6) See G. Herzberg, "Molecular Spectra and Molecular Structure, III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand, New York, N. Y., 1966.

(7) For a general discussion on excimer see J. B. Birks, "Photophysics," Wiley-Interscience, New York, N. Y., 1970.