ease with which triacanthine is cleaved by acid and by hydrogenolysis suggests that the double bond is allylic to the 7-nitrogen atom.[17] Dihydrotriacanthine is stable to the conditions under which triacanthine is cleaved by hydrochloric acid. The similarity between the ultraviolet spectra of triacanthine and dihydrotriacanthine shows that the double bond in triacanthine is not part of the chromophore.

Finally, n.m.r. spectra of triacanthine and dihydrotriacanthine (30% in liquid sulfur dioxide), in addition to the previously mentioned data, permit unambiguous assignment of structure I to triacanthine. Triacanthine shows a single unresolved peak in the CH$_3$-C region (τ = 8.13), from (CH$_3$)$_2$C=, and, in addition, a triplet (τ = 4.49) and a doublet (τ = 5.01)—a splitting pattern which is indicative of the =CH—CH$_2$— moiety. Dihydrotriacanthine exhibits a doublet (τ = 9.05) which came from the methyl groups in (CH$_3$)$_2$CH—.

Future publication will deal with the synthesis, the further chemistry of triacanthine, and the results of tests for biological activity.

[17] *Cf.* F. M. Dean in "Fortschritte der Chemie Organischer Naturstoffe," ed. by L. Zechmeister, **9**, 269 (1952), for the behavior of a γ,γ-dimethylallyl ether toward acid and catalytic hydrogenation.

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INTERMETALLIC COMPOUNDS OF ALKALI METALS WITH PLATINUM. A NOVEL PREPARATION OF A COLLOIDAL PLATINUM HYDROGENATION CATALYST

Sir:

We have found that *in vacuo* or under an atmosphere of argon, molten lithium and metallic platinum undergo a violently exothermic reaction having an ignition temperature of about 540°. X-Ray diffraction powder patterns of the resulting brittle, grayish product, taken after the excess lithium was removed by treatment with water or 3 *M* hydrochloric acid, showed broad lines whose intensities and positions were in good agreement with calculations based on an MgCu$_2$ cubic "Laves phase" lattice having $a_0 = 7.60 \pm 0.05$ Å. A flame photometric determination of the water-inactive lithium content of the reaction product (dissolved in *aqua regia*) showed over 85% of the theoretical amount required for LiPt$_2$ proportions. The combined lithium and platinum analyses account for over 99% of the product by weight. Because of the great disparity in the atomic weights, however, the lithium analysis is clearly the one which is most important as regards the identification of the species formed.

A few experimental details are given. Most of the reactions were carried out in a glass system with the reactants contained in molybdenum crucibles fitted with thermocouples. Molybdenum has been shown previously[1] to be inert to molten alkali metals. Nevertheless, several experiments were performed in which the platinum strip was bent in such a way that it fulfilled the dual roles of reactant and container, with results identical with those obtained by the alternative procedure. All cutting and transfer operations involving the lithium were made in a protective bath of pentane which ultimately was pumped off, along with the air in the system. Just prior to the ignition step, several flushings with argon also were made. In every case the surface of the lithium remained free of appreciable contamination throughout the entire cycle of operations.

The reactions normally were carried out on a 50–100 mg. scale with the lithium present in about a tenfold mole-excess. During the few minutes required to encompass the 200–500° temperature range, some physical attack on the platinum strip occurred. This particular phase of the process, which we do not believe involves a chemical reaction, is described more fully below. Somewhat above 500° a more spectacular phenomenon obtains. At some point, usually on the perimeter of the metal–liquid metal interface, we observe considerable agitation accompanied by a moderately intense, reddish glow. These effects spread rapidly over the entire contact area, and in less than a second the reaction is completed. During this short time some lithium distills (or perhaps spatters) rather uniformly onto the walls of the glass envelope, a traverse distance of about a centimeter. It is possible to remove the burner at the instant of ignition, and the effects we describe will proceed in an entirely self-sustaining fashion. Although we have not, as yet, examined this system calorimetrically, some relatively crude measurements indicate that the surface temperature of the crucible immediately below the reacting materials increases by several hundred degrees.

It is unlikely that contaminant amounts of lithium oxide or lithium hydroxide are responsible for the phenomenon, for we have used a burner to heat both of these compounds to bright-red incandescence in the presence of platinum, with no effects which in any way resemble those observed with the pure metals.

By heating the raw materials to about 650° in an argon atmosphere, we have also obtained, in poor yield, a sodium–platinum compound which is isostructural with LiPt$_2$, and hence probably is NaPt$_2$. This latter compound has a lattice parameter of 7.48 ± 0.02 Å. Our results complement those of Compton and collaborators,[2,3] who very recently identified a number of cubic Laves phase compounds containing noble metals in combination with both alkaline earth and rare earth elements.

We also have found that molten lithium, at temperatures well below that at which appreciable reaction occurs, has a remarkable ability to penetrate the platinum lattice. A similar type of attack, occurring near the melting point of lithium, has been noted previously by Grosse.[4] We have observed that, overnight, lithium will climb several centimeters up a platinum strip whose bottom is in contact with a lithium pool contained in a molybdenum crucible at 400°. Apparently a diffusive

[1] E. E. Hoffman and W. D. Manly in "Handling and Uses of the Alkali Metals," Advances in Chemistry Series No. 19, American Chemical Society, Washington, D. C., 1957, p. 82.

[2] E. A. Wood and V. B. Compton, *Acta Cryst.*, **11**, 429 (1958).

[3] V. B. Compton and B. T. Matthias, *ibid.*, **12**, 651 (1959).

[4] A. V. Grosse, *Z. Naturforsch.*, **8b**, 533 (1953).

mechanism rather than accretion from the gas phase is operating, for no attack on the strip was noted unless direct physical contact was made with the lithium melt. When one of these lithium-doped samples is treated with water or dilute acid, microdispersion occurs. If left undisturbed, these colloidal suspensions do not settle out for several hours. The final black product, which can be powdered easily and brushed through a 325-mesh screen, still contains ~ 1–1.5 weight per cent. lithium. "Hydrolysis" of platinum–lithium admixtures prepared at the lower temperatures proceeds with a vigor comparable to that found for lithium itself. By contrast, the excess lithium leaches out of the reacted preparations rather slowly. The reaction product, $LiPt_2$, even when crushed to a very fine powder, appears to be unaffected by prolonged exposure to water.

Apart from an occasional lithium hydroxide line, X-ray diffractometer studies on the black, colloidal material yield only the spacings of the platinum lattice, broadened to such an extent that the crystallites appear to have dimensions in the 50–100 Å. range. It should be noted that the residual lithium content of these disperse preparations is slightly smaller than that of the compound $LiPt_2$.

Although $LiPt_2$ itself is comparatively inactive, we have found many of the "unreacted" platinum–lithium preparations to be highly effective catalysts for the hydrogenation of olefins. For example, the hydrogenation of cyclohexene in acetic acid under one atmosphere hydrogen pressure at room temperature will proceed up to twice as rapidly with our dispersed platinum–lithium catalyst as with an equal weight of the supported platinum oxide catalyst PS 14.[5]

We are currently investigating techniques for preparing catalysts with reproducible activity, the selectivity of these catalysts, and intermetallic compound formation in other systems involving alkali and noble metals.

[5] F. A. Vandenheuvel, *Anal. Chem.*, **28**, 363 (1956).

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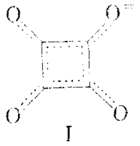
SYMMETRICAL RESONANCE STABILIZED ANIONS,[1] $C_nO_n^{-2}$

Sir:

Recently Cohen, Lacher and Park have described the interesting compound diketocyclobutenediol, and have suggested that it ionizes to give the symmetrical resonance-stabilized anion I.[2] We now wish to point out that anion I represents only one member of a general series of symmetrical electron-delocalized anions, $C_nO_n^{-2}$, salts of which may be considered as a new class of aromatic substances. We also wish to report observations on the next two higher members of the series, $C_5O_5^{-2}$ (II) and $C_6O_6^{-2}$ (III).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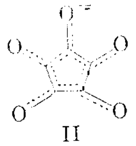
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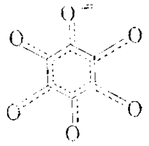
III

A symmetrical structure for the dianion of croconic acid, $C_5O_5^{-2}$, already has been proposed by Japanese workers on the basis of the infrared spectra of croconate salts.[3] Definite evidence for the symmetrical structure is now available from Raman spectral measurements. Five lines were observed in the Raman spectrum of an aqueous solution of dilithium croconate: polarized lines at 1718 and 641 cm.$^{-1}$, and depolarized lines at 1584, 1241, and 556 cm.$^{-1}$. The totally symmetrical (D_{5h}) structure should have six Raman active fundamentals, two polarized and four depolarized. Our results are inconsistent with any structures in which all the oxygen atoms are not equivalent, since such anions should have a minimum of nineteen Raman-active fundamental modes. Thus the croconate ion must have the fivefold symmetrical structure, II, in aqueous solution.

An anion $C_6O_6^{-2}$ is produced by ionization of the analytical indicator rhodizonic acid, $H_2C_6O_6$. The Raman spectrum of the rhodizonate anion was not determined on account of its deep orange color. However, the symmetrical aromatic structure (III) for this anion seems probable because of the similarity of the infrared spectrum to that of croconate anion. Like the dipotassium salt of I, both rhodizonate and croconate salts have no infrared absorption in the usual carbonyl region, but instead show a very strong and broad band centered near 1500 cm.$^{-1}$.[4]

Qualitative observations suggest that stabilization of the dianion relative to its acid decreases from $C_4O_4^{-2}$ to $C_5O_5^{-2}$ to $C_6O_6^{-2}$. Thus for instance the dissociation constants for the acids decline in this order.[5] Preliminary LCAO molecular orbital calculations[7] of the delocalization energy in symmetrical anions $C_nO_n^{-2}$ have been carried out, considering only interactions between adjacent atoms. Results indicate that the total delocalization energy increases as ring size increases from $C_3O_3^{-2}$ to $C_8O_8^{-2}$. However, delocalization energy *per atom* decreases in the same sequence. The unknown anion $C_3O_3^{-2}$ is predicted to have an

[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

[2] S. Cohen, J. R. Lacher and J. D. Park, THIS JOURNAL, **81**, 3480 (1959).

[3] K. Yamada, N. Mizuno and Y. Hirata, *Bull. Chem. Soc. Japan.*, **31**, 543 (1958); A. Washino, K. Yamada and Y. Kurita, *ibid.*, **31**, 552 (1958).

[4] An X-ray crystallographic investigation of the structure of dipotassium rhodizonate now is being carried out by L. F. Dahl and M. Neuman of these laboratories.

[5] Values of pK_1 and pK_2: for $H_2C_4O_4$,[2] ~ 1 and 2.2; for $H_2C_5O_5$,[6] 2.17 and 4.0; and for $H_2C_6O_6$,[6] 3.15 and 4.9.

[6] E. Carpeni, *J. chim. phys.*, **35**, 208 (1938); G. Schwarzenbach and H. Sutler, *Helv. chim. acta.*, **24**, 617 (1941).

[7] J. D. Roberts, A. Streitweiser, Jr., and C. M. Regan, THIS JOURNAL, **74**, 4579 (1952), to which the reader is referred for additional references to the method. Coulomb integrals for C and O were taken as α and $\alpha + 2\beta$, and resonance integrals for C–C and C–O as β and $\sqrt{2}\beta$, respectively, following R. D. Brown, *Quart. Revs.*, **6**, 63 (1952). See also E. J. Smutny, M. C. Caserio and J. D. Roberts, THIS JOURNAL, **82**, 1793 (1960).