that the C^{13} resonance signal of the hydroxyl-substituted carbon atom of salicylaldehyde and related hydroxyaromatic compounds with well-established intramolecular hydrogen bonds[14] occurs about 6 p.p.m. downfield from the value one would predict from simple additivity relations.[15]

At the present stage of our understanding of C^{13} shifts it is difficult to account with certainty for the postulated effect on the C^{13} spectrum of hydrogen bonding of phenol to solvent. However, a qualitative explanation can be formulated in terms of the following valence bond description of the complex in which phenol is hydrogen bonded to a base B (which may be either solvent or another phenol molecule in the case of self-association).
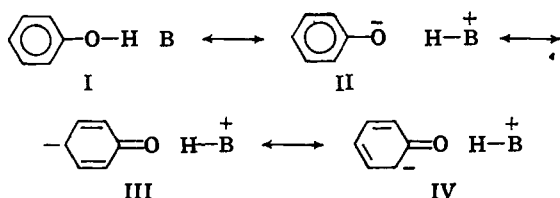
One would expect that the increasing basicity of solvent would increase the strength of the hydrogen bond between phenol and solvent, that is, increase the relative importance of canonical structures II, III, and IV. While a consideration of the charge densities implied by this description or by the inductive effects one might anticipate for hydrogen bonding is not immediately useful in interpreting the observed C^{13}-O shifts, the assumed effect on C-O bond order embodied in the valence-bond description may be illuminating. If one considers the chemical shift of the carbonyl carbon atom in p-benzoquinone, -59.4 p.p.m., as an indication of a value to be expected for the hypothetical chemical shift of the substituted carbon atom of structure III or IV, then the decrease of shift with increasing solvent basicity with respect to hydrogen bonding becomes understandable in terms of the increasing contribution of these structures to the valence-bond description of phenol. Of course, when the solvent basicity is increased to the point where appreciable concentrations of solvated phenoxide ion exist, then the hydrogen-bonding effect blends into, or is overshadowed by, the influence of the ion on the equilibrium-average shift which is observed. It is interesting that the changes in chemical shift experienced by the *ortho* and *para* carbons as the hydroxyl proton is removed by proton transfer to a strong base (ethoxide) are in opposite senses. We hope that further experiments with substituted phenols, additional solvents, and higher dilutions will allow a precise distinction to be made between the different interactions considered here and will provide a system with a wider range of shifts more suitable for the quantitative characterization of pertinent solvent properties.

(14) G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **68**, 437 (1964).
(15) G. B. Savitsky, *ibid.*, **67**, 2723 (1963).

DEPARTMENT OF CHEMISTRY   GARY E. MACIEL
UNIVERSITY OF CALIFORNIA   RONALD V. JAMES
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Stable Trianion Radicals

Sir:

Benzil readily accepts one or two electrons in discrete steps to form an anion radical (Bz_2^-) and dianion $(Bz_2^=)$, respectively.[1] An HMO calculation[2] gives the eigenvalue $E = \alpha$ (nonbonding) for the MO being filled in these reactions. More interesting is the fact that even at the dianion stage benzil has a vacant MO

TABLE I
HMO ENERGY LEVELS FOR PhCOCOPh

of not too high energy ($E = \alpha - 0.79\beta$) (see Table I). Recent work[3] led us to believe that coulombic repulsions in a trianion radical might not be extreme and accordingly it seemed possible that benzil might accept a third electron to form a novel trianion radical $(Bz_2^{\overline{\overline{\overline{}}}})$.

The red dianion of benzil (λ_{max} 470 mμ) is indeed converted to a purple trianion radical (λ_{max} 555 and 410 mμ) in 3 hr. by a 100% excess of potassium in refluxing THF. That the new species is a trianion radical is shown by its acid titer (triacidic base) and e.p.r. signal. A tetraanion could not be induced to form. Addition of 0.5 mole of benzil per mole of trianion radical, to convert the latter to the dianion stage, followed by treatment with excess benzoyl chloride, gave a 70% yield of 9,10-dibenzoyloxyphenanthrene. Anhydrous nickel chloride followed by benzoyl chloride gave the same ester in 60% yield. It appears that most of the trianion radicals have cyclized and lost hydrogen (molecular hydrogen is not evolved, however) forming the phenanthrenequinone trianion radical. The various oxidative treatments convert this to the dianion, which is dibenzoylated by added benzoyl chloride. This formulation is supported by the direct
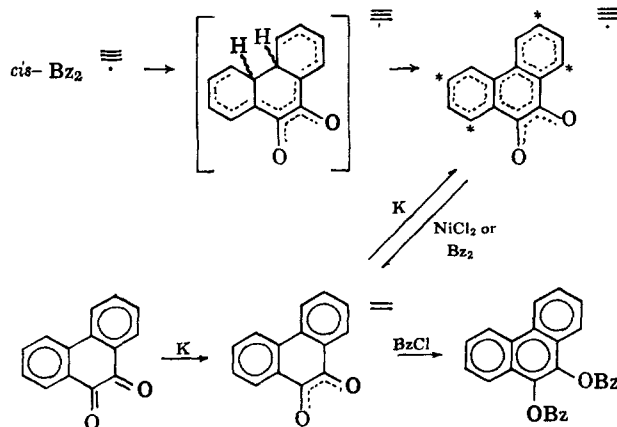
(1) H. Staudinger and A. Binkert, *Helv. Chim. Acta*, **5**, 702 (1922).
(2) Using parameters $\alpha_O = \alpha + 2\beta$, $\beta_{CO} = \beta\sqrt{2}$, and, where applicable, β_{Ph-C} (cross conjugation) $= 0.8\beta$.
(3) N. L. Bauld, *J. Am. Chem. Soc.*, **86**, 2305 (1964).

synthesis of the phenanthrenequinone trianion radical and comparison of its spectral properties with those of the trianion radical obtained from benzil. Thus, both routes produce a trianion radical which gives a five-line e.p.r. spectrum (coupling with the four starred protons) and absorbs in the visible region at 555 and 410 mμ.

The HMO calculations indicate that, whereas the NBMO being filled at the Bz_2^- and $Bz_2^=$ stages is predominantly an α-diketone MO, that which accommodates the third electron is largely of the cis-stilbene type, with high spin density on the phenyl rings at the ortho and para positions. The similar fate of $Bz_2^=$ and photoexcited cis-stilbenes[4] suggests a possible parallel between reactions of highly electronated and photoexcited molecules.

Calculations for the oxalate system also show an MO at $α - 0.73β$ which is vacant at the dianion stage. Again, excess potassium is found to convert the dianion, sodium oxalate, into a stable, purple trianion radical showing an e.p.r. singlet.

$$\text{O}\diagdown \!\! {}_C^{}\!\! {}^{,}\!C \!\! {}^{\diagup O}_{} \xrightarrow[\text{THF}]{K} \text{O}\diagdown \!\! {}_C^{}\!\! {}^{,}\!C \!\! {}^{\diagup O}_{}$$

A detailed report of the e.p.r. spectra of these and other trianion radicals will be forthcoming at a later date.

(4) R. Srinivasan and J. C. Powers, J. Am. Chem. Soc., **85**, 1355 (1963); F. B. Mallory, et al., ibid., **84**, 4361 (1962).

DEPARTMENT OF CHEMISTRY   NATHAN L. BAULD
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RECEIVED MAY 12, 1964

A Krypton Difluoride–Antimony Pentafluoride Complex[1]

Sir:

Krypton difluoride has recently been prepared in these laboratories by an electric discharge method.[2] This compound, though manifestly less stable than xenon difluoride,[3] might be expected to show an analogous chemistry. Recently it has been shown that xenon difluoride interacts with antimony pentafluoride to form a stable complex of composition $XeF_2 \cdot 2SbF_5$,[4] and now we report the preparation of the analogous complex $KrF_2 \cdot 2SbF_5$. The compound is formed by treating krypton difluoride with antimony pentafluoride in glass or Kel-F. Reaction is complete at −20°, and if excess antimony pentafluoride is present, most of the white crystalline material formed dissolves to give a clear yellowish solution at room temperature. The white complex can be recovered from the solution by pumping away the solvent at 25°. Two separate specimens gave the following analytical results: (1) sample weight 0.875 g.; Kr, 15.7%; Sb, 42.4%; and F, 41.9%; (2) sample weight 0.189 g.; Kr, 14.2%, Sb, 44.2%; and F, 41.6%. $KrF_2 \cdot 2SbF_5$ requires Kr, 15.1%; Sb, 43.8%; F, 41.0%.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.
(2) F. Schreiner, J. G. Malm, and J. C. Hindman, to be published.
(3) D. R. MacKenzie, Science, **141**, 1171 (1964).
(4) A. J. Edwards, J. H. Holloway, and R. D. Peacock, Proc. Chem. Soc., 275 (1963).

The complex $KrF_2 \cdot 2SbF_5$ is more stable and much less volatile than the parent difluoride. For example, a sample weighing 0.848 g. lost only 0.020 g. on pumping for 20 hr. at 25°. It melts at about 50°, but the liquid decomposes quickly to antimony pentafluoride, krypton, and fluorine. The complex also decomposes slowly in antimony pentafluoride solution at 25°. As expected, it is an extremely reactive material and ignites organic matter explosively. Solutions of $KrF_2 \cdot 2SbF_5$ in antimony pentafluoride appear to attack Kel-F. Aqueous hydrolysis in basic or slightly acidic solution yields not only the expected krypton and oxygen, but also appreciable quantities of fluorine monoxide. The infrared spectrum of the complex shows a strong characteristic absorption band at 813 cm.$^{-1}$ and other strong, poorly resolved absorptions in the 600–700 cm.$^{-1}$ region.

Preliminary experiments show that krypton difluoride combines with arsenic pentafluoride at −78°, but the adduct is very unstable and we have been unable to isolate it.

CHEMISTRY DIVISION   HENRY SELIG
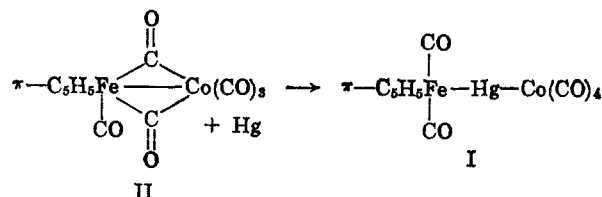ARGONNE NATIONAL LABORATORY   RAYMOND D. PEACOCK
ARGONNE, ILLINOIS

RECEIVED AUGUST 10, 1964

An Organometal Carbonyl Containing Covalent Bonds from Iron to Mercury to Cobalt

Sir:

Mercury salts of binuclear metal carbonyls, such as $Hg[Co(CO)_4]_2$,[1] $Hg[Mn(CO)_5]_2$,[2] and those of cyclopentadienyl derivatives of metal carbonyls, such as $Hg[\pi\text{-}C_5H_5M(CO)_n]_2$,[3,4] where $n = 2$ or 3 and $M =$ Mo, Cr, or Fe, are known. Although all of these compounds possess three metals covalently bonded, they are all symmetrical, consisting of two identical metal carbonyl portions bonded through mercury. For this reason they are usually referred to as mercury salts. In an extension of our mercury insertion reaction,[5] we have synthesized what is to the best of our knowledge the first example of a compound containing three different metals covalently bonded.

The new compound, π-cyclopentadienyldicarbonyliron mercury cobalt tetracarbonyl, $\pi\text{-}C_5H_5Fe(CO)_2\text{-}HgCo(CO)_4$ (I), was prepared by simply stirring a solution of π-cyclopentadienylmonocarbonyliron μ-dicarbonyl cobalt tricarbonyl[6] (II) in hexane with mercury under an atmosphere of carbon monoxide at room temperature for 48 hr.

$$\pi\text{-}C_5H_5Fe \underset{\underset{\underset{O}{\|}}{\underset{C}{|}}}{\overset{\overset{\overset{O}{\|}}{\overset{C}{|}}}{\diagup\!\!\!\!\diagdown}} Co(CO)_3 \; \longrightarrow \; \pi\text{-}C_5H_5Fe\!-\!Hg\!-\!Co(CO)_4$$

II   + Hg   I

On stirring, the dark red (almost black) solution very gradually changed to dark orange. The orange

(1) W. Hieber and H. Schulten, Z. anorg. allgem. Chem., **232**, 17 (1937).
(2) W. Hieber and W. Schropp, Jr., Chem. Ber., **93**, 455 (1960).
(3) E. O. Fischer, W. Hafner, and H. O. Stahl, Z. anorg. allgem. Chem., **282**, 47 (1955).
(4) E. O. Fischer and R. Böttcher, Z. Naturforsch., **10b**, 600 (1955).
(5) S. V. Dighe and M. Orchin, Inorg. Chem., **1**, 965 (1962).
(6) K. K. Joshi and P. L. Pauson, Z. Naturforsch., **17b**, 565 (1962).