As expected, acetonitrile solutions of Ia and Ib have instantaneous precipitates of silver bromide on treatment with silver nitrate reagent. More importantly, lithium aluminum hydride reduction of an ether suspension of Ia regenerated heptaphenyltropilidene in high yield.

The infrared spectra (KBr pellets) of the salts Ia and Ib (and the yellow bromination product before digestion or recrystallization) were closely similar to the spectrum of heptaphenyltropilidene (II) with three important differences: (i) in the C–H stretch region Ia and Ib show a single absorption band at 3040 cm.$^{-1}$, whereas II and other covalent heptaphenyltropyl derivatives have an additional absorption band at 2990–3000 cm.$^{-1}$ of slightly greater intensity; (ii) the major absorption band for the salts Ia and Ib occurs at 1325 and 1315 cm.$^{-1}$, respectively, a region in which II has only weak absorption; (iii) a strong absorption band observed at 760 ± 3 cm.$^{-1}$ for all covalent heptaphenyltropilidenes is totally absent in the spectra of Ia and Ib though the normal aromatic bands at 780, 720 and 695 cm.$^{-1}$ appear undisturbed. These relatively simple spectral changes offer strong support for the symmetrically delocalized ion represented in structure I.[5]

Addition of small amounts of water or methanol to dark red acetonitrile solutions of Ia (or Ib) resulted in rapid decolorization and the formation of, respectively, heptaphenyltropyl alcohol (IIIa), m.p. 233–236° (rapid heating[6]) (λ_{max}^{MeCN}, 258 (4.41), 293 (sh.) (4.16) mμ. *Anal.* Calcd. for $C_{49}H_{36}O$: C, 91.84; H, 5.66. Found: C, 91.96; H, 5.75), and methyl ether (IIIb), m.p. 229–232° (λ_{max}^{MeCN}, 256 (4.42), 293 (sh.) (4.14) mμ. *Anal.* Calcd. for $C_{50}H_{38}O$: C, 91.71; H, 5.85. Found: C, 91.92; H, 6.11), in good yield. Both covalent derivatives are excellent precursors of heptaphenyltropylium salts which they generate on treatment with the corresponding acid. Accordingly, fluoroboric acid in acetonitrile–acetic anhydride solvent quantitatively converted IIIa to the yellow-orange fluoroborate salt Ic, m.p. 267–272° (dec.) (λ_{max}^{MeCN}, 250 (4.98), 285 (sh.) (4.20) mμ. *Anal.* Calcd. for $C_{49}H_{35}BF_4$: C, 82.82; H, 4.96. Found: C, 82.77; H, 5.13). The infrared spectrum of Ic was identical in detail to the spectra of the other salts, Ia and Ib, except for the region 1025–1125 cm.$^{-1}$ where the fluoroborate ion absorbs strongly.

Solubility difficulties encountered with the salts of I have thus far prevented determination of a meaningful value of the pK_a of the heptaphenyltropylium ion; however, ultraviolet spectral studies have established that the pK_a of the unsubstituted tropylium ion is greater than that of the heptaphenyltropylium ion in 50% methanolic acetonitrile by at least 3 pK units. Thus, in this solvent, the unsubstituted tropyl methyl ether was ionized completely to tropyl cation by 0.01 N fluoroboric acid, while heptaphenyltropyl methyl ether was less than 10% ionized at 1 N concentrations of acid. In acetonitrile IIIb was converted entirely to cation I at 10^{-3} N and greater concentrations of fluoroboric acid.

Clearly, the substitution of phenyl groups for the hydrogens of the tropylium ion has decreased the stability of I, probably as a result of the increased importance of the phenyl inductive effect. Normally swamped by a much larger conjugative effect, the inductive effect becomes increasingly important in I as π-conjugation is disrupted by non-co-planarity of the seven phenyl rings with the tropylium ring. This inductive effect is probably the major factor affecting the relative stability of I and III since the extra resonance stabilization of I and the covalent heptaphenyltropyl derivative III due to the phenyls are not likely to be very different.[7]

Helpful discussions with Professor S. Winstein during the course of this work are gratefully acknowledged.

(5) Preliminary attempts to confirm this conclusion by proton magnetic resonance spectrometry were not successful because of the low solubilities of salts of I in the appropriate solvents.

(6) At moderate heating rates partial melting occurred at 215–220°, but no further change was noted up to 350°. Hexaphenylbenzene has been isolated from this thermal reaction in good yield as will be reported on later.

(7) Solvation factors will also affect this equilibrium between ionic and covalent forms; however, only a qualitative assessment of this effect can be made for a given solvent.

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RECEIVED AUGUST 21, 1961

REDUCTION OF SILVER AMINE COMPLEXES BY CARBON MONOXIDE

Sir:

The reduction of Ag^+ by CO in aqueous perchloric acid solution is very slow and attains measurable rates only at elevated temperatures (>100°) and pressures. We have found, however, that the addition of ammonia or of organic amines to the solution, to raise the pH and complex the silver ions, enhances the reactivity of the latter to a remarkable degree so that reduction proceeds readily at room temperature and atmospheric pressure. We report here the results of some preliminary kinetic measurements on these systems which suggest an explanation for this effect.

The experimental procedure was essentially similar to that employed in an earlier study[1] of the reduction of silver amines by H_2, except that the rates with CO were somewhat higher and, in most cases, the conditions employed correspondingly milder. In a typical experiment, CO at atmospheric pressure was bubbled through a solution, containing initially 0.01 M $AgClO_4$, 0.2 M CH_3NH_2 and 0.1 M $CH_3NH_3^+ClO_4^-$, at 25°; reduction to metallic silver proceeded smoothly with a half-time of about 40 min. In this and all the other kinetic experiments the concentration of free amine was sufficiently high so that the silver was present in solution predominantly as the diamine complex, AgL_2^+ (where L denotes amine). The over-all reaction under these conditions is thus represented by

$$2AgL_2^+ + CO + 2H_2O \longrightarrow 2Ag + CO_3^= + 4HL^+ \quad (1)$$

(1) J. Halpern and J. B. Milne, *Proc. 2nd Intern. Cong. Catalysis*, Paris, 1960, Vol. 1, p. 445.

For a number of amines including NH_3, $NH_2CH_2CH_2NH_2$, $C_2H_5NH_2$, CH_3NH_2 and $(C_2H_5)_2NH$, the rate-law was found to be

$$-d[CO]/dt = k_{exp}[CO][AgL_2^+][HL^+]^{-1} \quad (2)$$

which is kinetically equivalent to

$$-d[CO]/dt = k[CO][L\text{-}Ag\text{-}OH] \quad (3)$$

For the amines listed above, k_{exp} at 25° increased by a factor of about 140 in going along the series from NH_3 to $(C_2H_5)_2NH$. In each case the rate-determining reaction apparently was homogeneous and uninfluenced, at least over a considerable portion of the reaction, by the precipitated silver or other surface effects.

Evidence has been advanced[2] previously that the reduction of Hg^{2+} by CO in aqueous solution proceeds through an intermediate, $[—Hg—CO—OH]^+$, formed by "insertion" of CO between Hg^{2+} and a ligand water molecule, while analogous intermediates have been postulated in the Hg^{2+}- and Ag^+-catalyzed reduction of MnO_4^- by CO. It is noteworthy that the kinetics in the present instance also find a natural interpretation, according to the mechanism (4),(5), and (6), in terms of such an intermediate

$$AgL_2^+ + H_2O \underset{}{\overset{K}{\rightleftharpoons}} L\text{-}Ag\text{-}OH + HL^+ \quad \text{(Rapid equilibrium)} \quad (4)$$

$$L\text{-}Ag\text{-}OH + CO \xrightarrow{k} L\text{-}Ag\text{-}C(=O)\text{-}OH \quad \text{(Rate-determining)} \quad (5)$$

$$L\text{-}Ag\text{-}C(=O)\text{-}OH + L\text{-}Ag\text{-}OH \longrightarrow 2Ag + CO_3^{=} + 2HL^+ \quad \text{(Rapid)} \quad (6)$$

The apparent rate constant, k_{exp}, and the rate constant, k, defined by equation 5 are thus related through

$$k_{exp} = kK = kK_dK_bK_h \quad (7)$$

where K_d is the first dissociation constant of AgL_2^+ (*i.e.*, $AgL_2 \rightleftarrows AgL^+ + L$), K_b is the basicity constant of the amine (*i.e.*, $L + H_2O \rightleftarrows HL^+ + OH^-$) and K_h is the association constant of AgL^+ with OH^- ($AgL^+ + OH^- \rightleftarrows L\text{-}Ag\text{-}OH$). Table I reveals that for the series of monodentate amines examined, the variation in k_{exp} is accounted for in large measure by the variation in K_dK_b while the value of kK_h ($\sim 2 \times 10^5$) is relatively insensitive to the nature of L (the somewhat lower value for ethylenediamine is attributable to chelation effects). If K_h (which also is probably insensitive to the nature of L) is taken to be of the same order, *i.e.*, $\sim 2 \times 10^2$, as for the uncomplexed Ag^+ ion,[3] the value of k is found to be about 10^3 M^{-1} sec.$^{-1}$.

With NH_3 as ligand some departure from the kinetics described above was observed at high NH_4^+ concentrations when the kinetics approached the form predicted by the above mechanism under

$$-d[CO]/dt \propto [CO][AgL_2^+]^2[HL^+]^{-2} \quad (8)$$

(2) A. C. Harkness and J. Halpern, *J. Am. Chem. Soc.*, **83**, 1258 (1961).

(3) H. L. Johnston, F. Cuta and A. B. Garrett, *ibid.*, **55**, 2311 (1933); J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957, p. 69.

TABLE I

SUMMARY OF KINETIC AND RELATED THERMODYNAMIC DATA AT 25°

Amine (L)	k_{exp}, sec.$^{-1}$	$K_d \times 10^4$,[a] M	$K_b \times 10^4$,[a] M	$kK_h \times 10^{-5}$,[b] M^{-2} sec.$^{-1}$
NH_3	5.3×10^{-4}	1.2	0.18	2.5
$NH_2CH_2CH_2NH_2$	1.1×10^{-2}	12	1.5	0.61
$C_2H_5NH_2$	1.6×10^{-2}	1.2	6.4	2.1
CH_3NH_2	3.0×10^{-2}	3.0	5.2	1.9
$(C_2H_5)_2NH$	7.6×10^{-2}	5.0	9.1	1.7

[a] Values of K_d and K_b from ref. 4 corrected[1] where necessary to 25°. [b] Computed from $kK_h = k_{exp}/K_dK_b$.

conditions when (because of lowering of the concentration of L–Ag–OH by reverse displacement of equilibrium 4) reaction 6 is slowed down to the point where competition between this step and reversal of step 5 now determines the rate.

Among other things it would appear from these considerations that the increase in pH, rather than effects associated specifically with complexing of the Ag^+ ion, is primarily responsible for the markedly enhanced reactivity of the latter toward CO on going from acidic to amine-buffered media.

Support of this work by the Alfred P. Sloan Foundation and the National Research Council of Canada is gratefully acknowledged.

(4) "Stability Constants," Chemical Society Special Publications, No. 6 (1957), No. 7 (1958).

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RECEIVED AUGUST 25, 1961

REACTIVITY OF CYCLIC PEPTIDES. I. TRANSANNULAR HISTIDINE-O-ACETYLTYROSINE INTERACTION

Sir:

We have prepared *cyclo*-glycyl-L-histidylglycyl-L-tyrosylglycylglycyl as part of a program on side-chain reactivity in cyclic peptides. Reaction of this imidazole-containing peptide with one equivalent of *p*-nitro- or 2,4-dinitrophenyl acetate results in acylation of the phenolic oxygen and, as a consequence of imidazole-acetoxyphenyl coördination, virtually complete inhibition of further esterolytic activity. The interaction implied by this observation, requiring, as it does, 16-membered ring formation, would be unexpected in the absence of some secondary structure in the peptide molecule. Its occurrence in the present case suggests that cyclic peptides may be valuable models for study of protein side-chain interactions.

Cyclization, without especial dilution, of L-tyrosyltriglycyl-*im*-benzyl-L-histidylglycine, using ethyl-γ-dimethylaminopropylcarbodiimide in dimethylformamide, yielded 58% of the imidazole-blocked cyclic peptide, purified by partition chromatography using 2-butanol/water (4:1) on cellulose powder. Debenzylation was effected by brief treatment with sodium in liquid ammonia, and the final product was isolated as in the preceding step (37%). This material was chromatographically homogeneous in seven different solvent systems, ninhydrin inactive, and yielded only histidine, tyrosine and glycine on hydrolysis.