Pentacarbanilino-D-glucose Diethyl Mercaptal

To a solution of 3.0 g. (10.5 millimoles) of D-glucose diethyl mercaptal (m.p. 125°) in 75 ml. of dry pyridine, maintained at 100°, was added all at once 11.4 ml. (105 millimoles) of phenyl isocyanate. The mixture was stirred at 100° for 6.5 hours, cooled, and added to 300 ml. of absolute ethanol. This clear solution on dilution with an equal volume of water gave 9.1 g. (98.5% of the theoretical amount) of crude pentacarbanilino-D-glucose diethyl mercaptal. Two recrystallizations from hot *n*-butanol in the proportion of 50 ml. of solvent per gram of crude compound gave an analytically pure material melting at 207–210°, $[\alpha]^{26}D$ +41.8° (*c* 0.9, pyridine). Recovery of purified material was approximately 83% at each recrystallization step.

Anal. Calcd. for $C_{45}H_{47}N_5O_{10}S_2$: C, 61.3; H, 5.3; N, 7.9; S, 7.3. Found: C, 61.3; H, 5.5; N, 7.7; S, 7.3.

J. E. Hodge prepared the D-glucose diethyl mercaptal and C. H. Van Etten performed the microanalyses.

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RECEIVED JULY 30, 1951

COMMUNICATIONS TO THE EDITOR

RETENTION OF Br^{80} IN COMPLEX BROMIDES, FOLLOWING ISOMERIC TRANSITION[1]

Sir:

The 18 minute bromine nascent from the isomeric transition decay of Br^{*80} is known to possess a high chemical reactivity. Disruption of the parent molecule appears always to occur, in the case of aqueous bromate ion and of various organic bromides, although in pure condensed systems some recombination of the primary fragments has been postulated. This reactivity is due to the high positive charge on the bromine which results from the Auger ionization that follows internal conversion.[2] It seemed possible that a bromine-containing Werner complex might more easily tolerate such a positive increment in charge, especially if the complex ion were negative in sign to begin with. Results are here reported for $Co(NH_3)_5Br^{+2}$ and $PtBr_6^{-2}$.

The general procedure was to prepare a solution of the complex, labelled with 4.4 hour Br^{80} (in equilibrium with the 18 minute daughter), and then to precipitate the complex as bromopentamminecobaltate(III) nitrate or as ammonium bromoplatinate(IV). Sodium bromide, if not already present, was added before the separation. The degree of retention of the 18 minute isomer was determined from the growth curve of the precipitated complex. Retention in the solid state was determined by dissolving the solid complex, adding sodium bromide, and immediately reprecipitating the complex. Ordinary exchange of bromide ion with either complex was negligible in the *ca.* two hours time involved (in the dark).

Evidently, disruption of the bromopentamminecobaltate(III) ion occurred upon every isomeric transition, and without recombination of fragments or any re-entry of bromine into another molecule of complex. Recombination of primary fragments to give the original complex might be expected to be improbable since the complex ion is unstable in solution and aquates slowly; the process might be responsible for the small retention in the solid. Re-entry of the "hot" 18 minute bromine into a different molecule of complex would be unlikely in solution because of the low concentration of the complex.

The high retention by aqueous bromoplatinate(IV) ion cannot be due to re-entry, by the same argument as above, and also in view of the lack of dependence of the effect upon concentration and upon added free bromide ion. Furthermore, it seems unlikely that the retention was due to a recombination of primary fragments, again because the complex ion is unstable toward aquation. Interestingly, the same high retention was observed when free bromide ion was initially present, indicating that isomeric transition did not so activate the complex as to permit exchange.

These results suggest that the degree of reactivity induced by isomeric transition is strongly dependent upon the charge of the parent molecule, but the two complex ions studied are too dissimilar for this conclusion to be more than tentative. Further work on this and related systems is in progress.

TABLE I

Complex	Concn. of complex, *M*	% retention	
$Co(NH_3)_5Br^{+2}$	0.01	0	
$[Co(NH_3)_5Br](NO_3)_2$	(solid)	14	
$PtBr_6^{-2}$	0.00166	52	52
	0.0005	70[a]	53
	0.0005 with 0.003 *M* NaBr	54	
$(NH_4)_2PtBr_6$	(solid)	100	

[a] Possibly some photocatalyzed exchange.

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RECEIVED AUGUST 28, 1951

STERIC INHIBITION OF HYPERCONJUGATION

Sir:

For *p*-alkylbenzhydryl chlorides, the first order rates of solvolysis decrease in the order $CH_3 > CH_3CH_2 > (CH_3)_2CH > (CH_3)_3C$. Stabilization

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[1] This work was carried out under contract N6onr23809 between the University of Southern California and the Office of Naval Research.

[2] For a recent bibliography see S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951).