We have studied the reaction of chlorine in dry acetic acid on methyl α-D-glucopyranoside. The reaction mixture after removal of any acetyl groups with aqueous potassium carbonate was separated by chromatography on thick paper into D-glucose (52%), unreacted methyl α-D-glucopyranoside (22%), and a third fraction (26%) which is a mixture containing 1,6-anhydro-β-D-glucopyranose and an unknown material. Acetylation of the mixture gave 1,6-anhydro-2,3,4-tri-*O*-acetyl-β-D-glucopyranose together with an unidentified acetate.

In a similar oxidation of maltose, D-glucose was again the major nonacidic product, and 1,6-anhydro-β-D-glucopyranose was formed in small amounts.

The formation of these reaction products can be rationalized in terms of the proposed intermediate glucosyl chloride (III) undergoing solvolysis in acetic acid to give 1-*O*-acetyl-D-glucopyranose (IV) and also dehydrohalogenation to give 1,6-anhydro-β-D-glucopyranose (V), probably *via* 1,2-anhydro-α-D-glucopyranose.[8]

The oxidation products from anhydrous amylose and chlorine in dry acetic acid also support the proposed mechanism. Chlorinolysis of the 1→4 links followed by reduction with borohydride produces terminal D-galactose residues. Subsequent hydrolysis and reduction to the alditols, and separation of their acetyl derivatives, gave hexaacetylgalactitol and hexaacetyl-D-glucitol. The formation of D-galactose by reduction of the oxidized amylose indicates the presence of a 4-keto end group,[9] which is produced by dehydrohalogenation of the first formed D-glucose 4-hypochlorite.

The above mechanism also explains the major products of oxidation of glycosides with chlorine in an aqueous medium. The glycosyl chloride (III) would be solvolyzed to the aldose which is converted to an aldonolactone by oxidation analogous to the aqueous bromine oxidation of D-glucose to D-glucono-δ-lactone.[10-12]

(8) J. Janson and B. Lindberg, *Acta Chem. Scand.*, **13**, 138 (1959).
(9) O. Theander, *ibid.*, **12**, 1883 (1958).
(10) H. S. Isbell and C. S. Hudson, *Bur. Std. J. Res.*, **8**, 327 (1932).
(11) H. S. Isbell, *J. Res. Natl. Bur. Std.*, **66A**, 233, (1962).
(12) I. R. L. Barker, W. G. Overend, and C. W. Rees, *J. Chem. Soc.*, 3254 (1964).

Roy L. Whistler, T. W. Mittag, T. R. Ingle
Department of Biochemistry
Purdue University, Lafayette, Indiana
Received July 26, 1965

Mechanisms of Photochemical Reactions in Solution. XXX.[1] Photosensitized Isomerization of Azobenzene

Sir:

We have investigated the photosensitized isomerization of azobenzene in isooctane in order to shed further light on the mechanism of the reaction. The choice of suitable sensitizers for these experiments was critical. Azobenzene absorbs light in both the ultraviolet and visible regions of the spectrum, and as a result filters had to be used to exclude the visible radiation. Those sensitizers with a significant quantum yield for fluorescence could not be used because of the possibility that azobenzene might absorb this fluorescent radiation. Similarly, sensitizers excited through n–π* transitions could not be used because the excited states of these sensitizers abstracted hydrogen from the hydrocarbon solvent at a significant rate. The radicals so produced react with the azo linkage of the azobenzene.[2] Sensitizers exhibiting high extinction coefficients above 400 mμ were not used because the 400–450 mμ region of the spectrum was used for azobenzene analysis. Table I lists sensitizers with triplet energies varying from 45 to 66.6 kcal./mole,[3] which were used to effect photoisomerization of azobenzene. The photostationary states were established from both directions. Within experimental error the same stationary state was obtained with each of these sensitizers, indicating that a sensitizer with triplet energy of ~45 kcal./mole still behaves as a high-energy sensitizer with regard to energy transfer to azobenzene.

(1) Part XXIX is A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, **4**, 259 (1965).

Table I. Photostationary States for Photosensitized Isomerization of Azobenzene

Sensitizer	E_t	*cis*, %
3-Acetylpyrene	~45	1.8
β-Acetonaphthone	59.3	1.5
Triphenylene	66.6	1.6

This latter fact was further substantiated by measurement of the rates of energy transfer from the sensitizers to azobenzene by flash spectroscopy. Using a kinetic analysis based on the reasonable assumption that at low azobenzene concentration the photostationary state is established after only two or three flashes of light, it was found that the energy-transfer step (to either *cis*- or *trans*-azobenzene) was probably diffusion controlled.[4] The rate constants for the energy transfer process are given in Table II.

Table II. Rates of Quenching of Sensitizer Excited States by Azobenzene

Sensitizer	E_t	k_q, M^{-1} sec.$^{-1}$
3-Acetylpyrene	45	4.0×10^9
β-Acetonaphthone	59.3	3.4×10^9

The results are reminiscent of those encountered in the study of the sensitized isomerization of the stilbenes and 1,2-diphenylpropenes[5] where it was also found that high-energy sensitizers produce the same photostationary states with either substrate. These results can be understood if transfer of energy to either stereoisomeric ground state leads to formation of a common excited state (or states) from which decay to ground-state molecules occurs. An abbreviated mechanism is

$$S^{*(3)} + \textit{trans}\text{-A} \xrightarrow{k_1} S + A_T \quad (1)$$

$$S^{*(3)} + \textit{cis}\text{-A} \xrightarrow{k_2} S + A_T \quad (2)$$

$$A_T \xrightarrow{k_3} \textit{trans}\text{-A} \quad (3)$$

$$A_T \xrightarrow{k_4} \textit{cis}\text{-A} \quad (4)$$

At the stationary state

$$\frac{[trans]_s}{[cis]_s} = \frac{k_2 k_3}{k_1 k_4} \quad (5)$$

(2) J. K. S. Wan, L. D. Hess, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **86**, 2069 (1964).
(3) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).
(4) For discussion of a probable limitation on the significance of "diffusion control" see R. M. Noyes, *ibid.*, **86**, 4529 (1964).
(5) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

Since triplet transfer to either isomer is diffusion controlled, the excitation ratio, k_2/k_1, should be unity for high-energy sensitizers so that the isomer ratio in the photostationary state is a direct measure of the decay ratio, k_3/k_4. This provides a means for comparison of the mechanisms of the direct and sensitized reactions. If excitation by direct absorption of light is followed by quantitative crossing into the triplet system, the decay ratio should be the same for the two processes. Since the excitation ratio for direct irradiation is just the ratio of the molar extinction coefficients for the two isomers, the photostationary state relationship becomes

$$\frac{[trans]_s}{[cis]_s} = \frac{\epsilon_{cis}k_3}{\epsilon_{trans}k_4}$$

The predicted relationship was found to hold in the case of the olefinic substrates studied previously,[5] but does not hold for the azobenzenes. The value of k_3/k_4 measured by photosensitization is about 60. Zimmerman[6] measured the decay ratio for azobenzenes as a function of wave length and found a value of 4 for π–π^* excitation and a value of 2 for n–π^* excitation. The difference between the two numbers is itself an indication that crossing to triplets is not the sole fate of excited singlets. The very large difference between the decay factor for the sensitized reaction and either number for the direct process shows clearly that decay from singlets does not involve passage through the lowest triplet state of the system. The difference between the results also seems to rule out the possibility that *both* singlet and triplet electronically excited states decay by way of highly vibrationally excited forms of the electronic ground states. Since the sum of the quantum yields for the *cis* → *trans* and *trans* → *cis* processes is high,[6] the results cannot be explained by a mechanism involving inefficient inter-system crossing with isomerization occurring only in those molecules that become triplets. Most of the reaction probably involves isomerization of excited singlets themselves, either while they are excited or during the act of internal conversion to ground singlets. Mechanisms involving crossing of excited singlets to higher triplets are unattractive because of the speed with which such species would be expected to decay the lowest triplet.

Acknowledgment. This study was supported by the National Science Foundation.

(6) G. Zimmerman, L. Chow, and U. Paik, *J. Am. Chem. Soc.*, 80, 3528 (1958).

(7) National Science Foundation Postdoctoral Fellow, 1964.

Lee B. Jones,[7] George S. Hammond
Contribution No. 3216, Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California
Received March 8, 1965

Classification of Alcohols by Nuclear Magnetic Resonance Spectroscopy. A Cautionary Note

Sir:

A recent communication described a clever method for classification of alcohols by nuclear magnetic resonance spectroscopy.[1] The authors reported that in "dimethyl sulfoxide solution strong hydrogen bonding to the solvent shifts the hydroxyl resonance downfield (τ 6.0 or lower) and reduces the rate of proton exchange sufficiently to permit observation of hydroxyl proton splitting." Although the communication reported that strong acids and bases remove the hydroxyl splitting, traces of acids, which catalyze exchange in the common n.m.r. solvents and are otherwise undetected, are clearly not expected to complicate the n.m.r. data with dimethyl sulfoxide (DMSO) solutions.

Attempting to apply this method to some substituted alcohols of interest to us,[2] we have found it unreliable for a number of alcohols with strong electron-withdrawing substituents close to the hydroxyl group. In the absence of special treatment of these alcohols with solid sodium or potassium carbonate,[4] and sometimes in spite of it, the n.m.r. spectra of DMSO solutions of these alcohols show loss of multiplicity of both hydroxyl and methylene resonances.

The alcohols used were freshly distilled; contamination in them was not revealed by gas chromatography. Those alcohols which failed to give the expected multiplet signals for O*H* were stored over solid carbonate for about 1 hr., with frequent shaking, and then used to prepare fresh DMSO solutions.

Alcohols of unequivocal structure which we have examined, together with chemical shifts (in p.p.m.) for hydroxyl proton,[5] include: (A) those giving expected multiplicity without special treatment: 2-ethoxyethanol (−4.55), allyl alcohol (−4.71), and *trans*-2-chlorocyclooctanol[6] (−4.92). (B) those giving expected multiplicity only after prior treatment with carbonate: 2-chloroethanol (−5.05) and 2-bromoethanol (−5.10) (freshly prepared DMSO solutions of 2-bromoethanol which gave the expected triplet signal deteriorated with time and after 1–2 hr. gave a broad singlet for hydroxyl proton (−5.10)). (C) those for which only sharp singlet (s) or smooth broad (b) signals for O*H* were obtained, even after treatment with carbonate: 2-cyanoethanol (−4.21, b), *trans*-2-bromocyclooctanol[6,7] (−4.60, s), ethyl lactate (−5.22, b), and 2,2,2-trichloroethanol (−5.71, s).[8]

The relative chemical shifts of the O*H* resonances in the various alcohols suggest a fair correlation with the relative electron-attracting power of the substituent. A comparison of relative positions for the 2-haloethanols with those for the 2-halocyclooctanols, however,

(1) O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

(2) Correspondence initiated by Dr. Gordon H. Whitham, of the University of Birmingham, England, about the identity of methylenecyclohexene bromohydrin[3] prompted the investigation reported here. We acknowledge appreciatively the exchange of information and ideas with Dr. Whitham, who has written that he has confirmed our observations that the hydroxyl proton signal is a singlet with DMSO solution of ethylene bromohydrin.

(3) J. G. Traynham and O. S. Pascual, *Tetrahedron*, 7, 165 (1959).

(4) Professor O. L. Chapman, serving as a referee for this communication, suggested the treatment with solid potassium carbonate to remove traces of acids.

(5) All spectra were obtained for dimethyl sulfoxide solutions approximately 10–30 vol. % in alcohol with a Varian Associates HA-60 spectrometer. Some dependence of chemical shift on concentration and on age of solutions was noted. Chemical shifts reported are for freshly prepared 10 vol. % solutions and are in p.p.m. relative to internal tetramethylsilane.

(6) J. G. Traynham and J. Schneller, *J. Am. Chem. Soc.*, 87, 2398 (1965).

(7) This compound was available in sufficient quantity for one experiment only; it was not treated with carbonate.

(8) Ethyl lactate, 2-cyanoethanol, and 2,2,2-trichloroethanol were also stored over potassium carbonate for 3 days. The O*H* signals recorded with DMSO solutions of these samples were shifted slightly from those obtained with samples treated for 1 hr. with carbonate, but the signals were little changed in appearance.