is expected on the basis of the intensity of adsorbed light being directly proportional to the concentration for the short light paths used.

To relate the CO yield to the oxalate decomposition, large scale experiments using 20 ml. of actinometer solution, 9.5×10^{-4} M uranyl oxalate and 9.5×10^{-3} M oxalic acid, were carried out. Oxalate decomposition was determined by titration with $KMnO_4$, and CO formation was determined by a combination of volume measurement and chromatography.

Oxalate decomposed, %	63	61	29
Oxalate dec./CO formed	3.7	3.3	3.4

Using a quantum yield of 0.60 for oxalate decomposed[6] and the average mole ratio given above, a quantum yield of 0.17 ± 0.02 is established for CO formation in the actinometer solutions used. Comparisons of the sensitivity of our method with some other actinometers are given in Table I.

TABLE I

COMPARISON OF ACTINOMETER SENSITIVITIES

Uranyl oxalate (titration)	6×10^{17}
Uranyl oxalate (colorimetric)[2]	3×10^{16}
Malachite green leucocyanide[3]	6×10^{14}
Uranyl oxalate (CO)	2×10^{14}

The improved speed, simplicity, and accuracy of a method which does not relay on the consumption of a reactant, but on the formation of an easily detected substance such as carbon monoxide, may be useful for a variety of purposes. For our work the great sensitivity enabled us to work with very small volumes, and it may also be utilized to reduce otherwise prolonged exposure times or to monitor the output of weak sources.

We consider that, with suitable calibration, the use of uranyl oxalate in the manner described above provides the most sensitive chemical actinometer presently available.

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THE STEREOCHEMISTRY OF THE POLAR ADDITION OF HYDROGEN BROMIDE TO ACENAPHTHYLENE

Sir:

While the stereochemistry of the free radical addition of hydrogen bromide to olefins has been studied extensively,[1,2] the polar addition of hydrogen halides has received little attention. Hammond and co-workers have found that addition of hydrogen bromide to 1,2-dimethylcyclohexene[3] and of hydrogen chloride to 1,2-dimethylcyclopentene[4] gives predominantly the *trans*-addition product. Hammond suggests that these results may be accommodated either by assuming that a π-complex intermediate intervenes which collapses on attack by a molecule of hydrogen halide, or by a completely concerted process in which hydrogen and halogen form bonds simultaneously from opposite sides of the olefin plane.

The observation of predominant *trans*-addition does not necessarily rule out a two-step mechanism involving a classical carbonium ion since steric factors in the intermediate ion may favor *trans*-addition. The reasoning involved[5] requires that the second step of the addition proceed faster than rotation about the C–C bond so that *trans*-attack would lead to a product in a staggered configuration whereas *cis*-attack would give a product in the unfavored eclipsed configuration. Such an "eclipsing" effect is most easily visualized for aliphatic olefins, but the effects would still be present in the cyclic systems studied by Hammond.

It would be desirable to study addition to an olefin in which steric effects do not favor one mode of addition over the other. Addition of deuterium bromide to acenaphthylene meets this criterion. In addition, this study provides an extreme test for the π-complex mechanism since a classical ion would be resonance-stabilized while the π-complex would be destabilized by the strain present in the five-membered ring. The fact that chlorine adds *cis* to acenaphthylene[6] in contrast to the usually observed *trans*-addition may reflect such destabilization of π-complexes in acenaphthylene.

We find that *deuterium bromide adds to acenaphthylene to yield more than 85% of the cis-addition product.* This result rules out a π-complex in the product-determining step. Formation of an ion pair intermediate, which collapses before the bromide ion can assume an orientation *trans* to the initially formed C–D bond, could account for the predominant *cis*-addition. Alternatively, a one-step concerted mechanism in which C–D and C–Br bonds are formed simultaneously on the same side of the olefin plane would lead to a *cis*-addition product.

Additions were carried out by passing deuterium bromide through a solution of acenaphthylene in methylene chloride at −60°. The product was isolated as a white crystalline solid, m.p. 68–9°, after crystallization from petrol ether. When the bromide was treated with potassium *tert*-butoxide in *tert*-butyl alcohol, acenaphthylene was obtained which was shown by n.m.r. analysis[7] to contain $95 \pm 10\%$ of deuterium in the 1-position. It may be safely assumed that the elimination reaction is stereospecifically *trans* since *trans*-elimination has been shown to be 740 times faster than *cis*-elimination for the 1,2-dichloroacenaphthylenes.[6] It fol-

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[1] H. L. Goering and D. W. Larson, *J. Am. Chem. Soc.*, **81**, 5937 (1959).

[2] P. S. Skell and R. G. Allen, *ibid.*, **81**, 5383 (1959).

[3] G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954).

[4] G. S. Hammond and C. H. Collins, *ibid.*, **82**, 5323 (1960).

[5] An analogous argument has been given by Goering to explain *trans* free radical addition of hydrogen bromide.

[6] S. J. Cristol, F. R. Stermitz and P. S. Ramey, *ibid.*, **78**, 4939 (1956).

[7] N.m.r. spectra were measured on a Varian high-resolution spectrometer V-4300B operating to 40 Mc./sec. and equipped with a Varian Field Stabilizer. Chemical shift values and coupling constants were determined to an accuracy of ±0.01 and ±0.2 c.p.s., respectively. The amount of deuterium present in the acenaphthylene obtained in the elimination reaction was determined as the difference between the number of protons found in authentic acenaphthylene (2.00) and the number of protons found in the unknown sample by integrated intensity measurement. A total of twenty-one determinations were made on the products of three different elimination reactions.

lows that the addition must have been more than 85% *cis*.

Since the reaction was rapid in the absence of light at −60°, and since styrene was found to add hydrogen bromide in the presence of acenaphthylene under identical conditions to give exclusively (2-bromoethyl)-benzene, the reaction cannot involve a radical mechanism. The identity of the styrene hydrobromide was established by n.m.r. analysis.

N.m.r. studies[7] confirm the above results. The bromide obtained from addition of deuterium bromide to acenaphthylene gives an n.m.r. spectrum with a complex multiplet extending from 2 τ to 3 τ, a doublet at 4.25 τ with a splitting of 7.4 c.p.s., and an unresolved broad signal at 6.15 τ. When this bromide is treated with lithium bromide in acetone, a significant change in the spectrum takes place. The signal at 4.25 τ becomes four lines of nearly equal intensity. The outer lines correspond with the original doublet while the inner lines are separated by 1.9 c.p.s.. Assignment of the 7.4 c.p.s. and 1.9 c.p.s. coupling to the *cis*- and *trans*-orientation of protons is consistent with the theoretical[8] and experimental[9] couplings found for dihedral angles of about 0° and 120°, respectively. Further verification is obtained when hydrogen bromide is added to the acenaphthylene containing >85% deuterium in the 1-position. The n.m.r. spectrum of the bromide in this case shows two strong lines at 4.25 τ separated by 1.9 c.p.s. Weak signals could also be detected corresponding to the 7.4 c.p.s. splitting.

It was possible to estimate from integrated peak intensities that no less than 85% of the *cis*-addition product was obtained. This is consistent with the results obtained from the elimination reaction. Similar results were obtained for addition reactions carried out in petroleum ether and pentane. We are currently investigating additions to other olefins and with other hydrogen halides in order to evaluate the various factors which determine the stereochemistry of the process.

(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(9) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).
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THE PREPARATION AND CHARACTERIZATION OF A COMPOUND CONTAINING TETRANITRATOCOBALTATE(II)

Sir:

We wish to report the preparation and characterization of a compound which is novel and interesting in two respects. The compound is tetramethylammonium tetranitratocobaltate(II), $[N(CH_3)_4]_2[Co(ONO_2)_4]$. This hygroscopic, violet compound was prepared by dissolving $[N(CH_3)_4]NO_3$ and $Co(No_3)_2\ 2H_2O$ in 2:1 mole ratio in nitromethane. On addition of chloroform, the product separated in a crystalline state, and was filtered, washed with chloroform and dried in vacuum.

Anal. Calcd. for $C_8H_{24}CoN_6O_{12}$: C, 21.1; H, 5.3; N, 18.4. Found: C, 20.9; H, 5.5; N, 17.9.

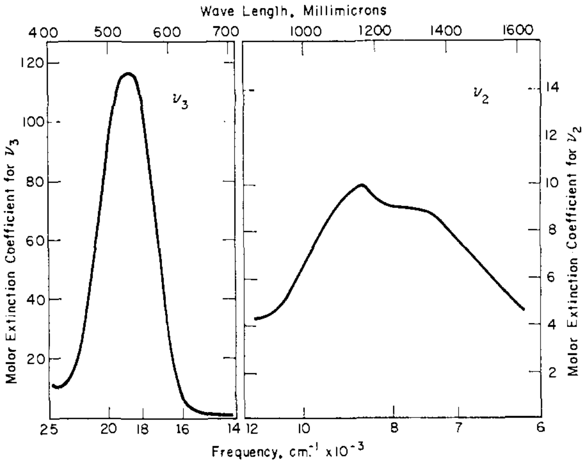

Fig. 1.—The visible and near infrared spectrum of $[N(CH_3)_4]_2[Co(ONO_2)_4]$, 0.01 molar, in acetonitrile containing 7.6×10^{-2} mole liter^{-1} of $[(C_6H_5)_3(n\text{-}C_4H_9)P]NO_3$. The mean energies of the absorption bands have been taken as 18,700 and 8,100 cm.$^{-1}$.

The infrared spectrum (mull) shows all of the bands characteristic of coördinated nitrate ions[1] (*i.e.*, M-ONO_2) and no others which cannot be assigned to the $[N(CH_3)_4]^+$ ions, thus supporting the view that all nitrate ions are coördinated to give $[Co(ONO_2)_4]^{2-}$ in the crystalline compound. There is also evidence that the same complex anions are present in acetonitrile solutions of the compound. Thus the molar conductance of a 0.003 molar solution in acetonitrile at 25° was 285 ohm^{-1} mole^{-1} which may be compared with a value of 266 ohm^{-1} mole^{-1} for a 0.003 molar solution of $[N(CH_3)_4]_2[Co(NCS)_4]$ in the same solvent. The infrared spectrum of a 0.1 molar solution in acetonitrile showed bands characteristic of coördinated nitrate ions. There were also very weak bands attributable to uncoördinated nitrate ions, indicating that slight dissociation of the complex anion occurs in this solvent.

The electronic absorption spectrum was recorded with successively increased additions of $[(C_6H_5)_3(n\text{-}C_4H_9)P]NO_3$ in order to repress dissociation of the complex anion. It was found that the spectra of 0.01 molar solutions in acetonitrile were identical for all phosphonium nitrate concentrations equal to or greater than 0.01 molar although the spectra of such solutions differed slightly, mainly in band intensities, from that of a solution containing only the cobalt compound. The spectrum is shown in Fig. 1.

The magnetic moment of $[N(CH_3)_4]_2[Co(ONO_2)_4]$ is 4.50 ±0.05 B.M. (calculated from susceptibility data with corrections for diamagnetism and temperature - independent paramagnetism[2]) which strongly implies[2] that the Co(II) is in a tetrahedral environment.

This compound is of interest since, to the best of our knowledge, it constitutes the first reasonably well-authenticated example of a compound con-

(1) B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).
(2) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).