the process leading to interchange of *cis* and *trans* methyl groups.[7]

If an appreciable amount of α,α-dimethylallylmagnesium bromide were present in the solutions, a decrease in temperature would be expected to result in an increase in concentration of the more stable γ,γ-dimethylallyl isomer. The temperature independence of this doublet and of the high-field doublet of the related butenyl Grignard reagent indicates that these Grignard reagents exist almost exclusively as the primary isomers.

[7] The magnitude of the uncertainty in these values reflects difficulties in obtaining an accurate value for the relaxation time T_2 of the methyl protons.

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RECEIVED MARCH 7, 1962

URANYL OXALATE ACTINOMETER FOR MICROPHOTOCHEMISTRY[1]

Sir:

Recently we have been studying photochemical reactions in aqueous solutions using volumes in the range of 1 to 10 microliters. After ultraviolet irradiation in sealed 1 mm. quartz tubes, about the size of melting point tubes, the cell is crushed and the entire sample vaporized into the carrier gas stream of a flame ionization gas chromatograph apparatus for analysis. For use with this technique, a suitable actinometric system was necessary. Consequently, we have developed a simplified method of uranyl oxalate actinometry based on the carbon monoxide formed rather than on the oxalate destroyed. The method is some 50 to 1000 times more sensitive than colorimetric or titration methods[2] and about three times as sensitive as the malachite green leucocyanide actinometer.[3]

Using the cells described above for actinometry, it is impossible to titrate the solutions for undecomposed oxalate. In our experiments, the concentration of uranyl oxalate was about 10^{-3} M to give the same optical density as the photochemical systems used, as required by Claesson's method of equivalent optical densities.[4,5] Consideration of the volumes involved and a suitable concentration change in the actinometer solution leads to the conclusion that the analytical method must be adequate for approximately 10^{-9} mole amounts, clearly outside the titration or colorimetric method range.

The reaction usually given[6] for the photodecomposition of oxalic acid in uranyl oxalate actinometry is

$$H_2C_2O_4 \longrightarrow H_2O + CO_2 + CO \tag{1}$$

From the equation, it appears that it should be possible to relate the amount of CO to the oxalate destroyed and, hence, to the light absorbed.

This reaction does not, however, represent the experimentally determined stoichiometry. Carter and Weiss[7] consider also the reactions

$$H_2C_2O_4 \longrightarrow HCOOH + CO_2 \tag{2}$$

$$H_2C_2O_4 + U^{6} \longrightarrow H_2O + 2CO_2 + U^{4} \tag{3}$$

They observed that the relative proportions of the three reactions depend upon the acidity of the solution and upon the concentration of quenching ions present. Nevertheless, it may be concluded that it should be possible to establish a relationship between the quantum yield of CO formation and that of oxalate decomposition.

In our experiments, 10 microliter samples of uranyl oxalate solution containing a 10-fold excess of oxalic acid were sealed in the 1 mm. quartz reaction tubes. The tubes were maintained in a water thermostat at 30.0° and subjected to 2537 Å. radiation from a mercury resonance arc. The tubes were crushed and the contents were swept into a 5 Å. molecular sieve[8] gas chromatographic column. CO was determined at these low levels by a flame ionization detector after catalytic hydrogenation to methane.[9]

Experiments were performed to determine the effect of irradiation time and concentration on CO formation. With an initial concentration of 9.5×10^{-4} M uranyl oxalate, the quantum yield of CO formation was found to be independent of time up to 60% decomposition of the oxalate. The rate of carbon monoxide formation was found to be linearly dependent on concentration, Fig. 1. This result

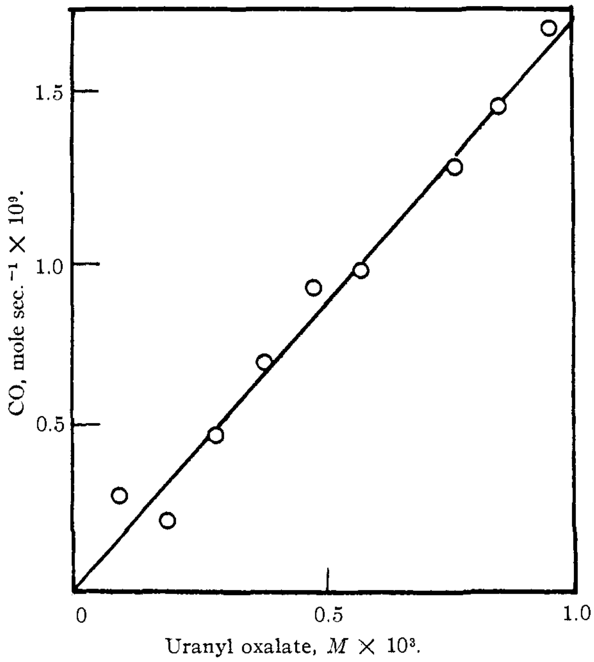

Fig. 1.—Rate of carbon monoxide formation as a function of uranyl oxalate concentration.

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[1] This research was supported by a grant from the U. S. Army Research Office (Durham).

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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[8]	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 ± 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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[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.