Isomerization of Chloride (VIa). A sample of chloride (VIa) isolated by preparative gas-liquid chromatography in an equal volume of dry diglyme with excess CsCl was heated at 95°C for 1 h to give a mixture containing 10% (Va) and 90% (VIa) as indicated by gas-liquid chromatography.

Reaction of Fluorosulfate (II) with CsF. A sample of 7.6 g (20 mmoles) (II) was added with stirring to 6 g (40 mmoles) anhydrous CsF and 15 ml dry diglyme. The reaction mixture was then heated for 15 min at 60°C. Distillation at 60-120°C gave 5.2 g of a mixture containing 39% (II), 45% (III), and 15% (VII) as indicated by gas-liquid chromatography and ^{19}F NMR spectroscopy. Further fractionation gave 3.8 g (80%) of a 3.6:1 mixture of (III) and (VII), which, upon treatment with excess CsF in diglyme, was completely converted to dimer (III) as indicated by gas-liquid chromatography and ^{19}F NMR spectroscopy [4].

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PHOTOOXIDATION OF ALKANES BY OXYGEN CATALYZED BY $CuCl_2$ IN ACETONITRILE

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The irradiation of a solution of anhydrous $CuCl_2$, taken as a photocatalyst, and an alkane in acetonitrile in the air with visible light ($\lambda > 320$ nm) leads to the formation of alcohol and ketone products.

Cyclohexane, hexane, and methane are oxidized to the corresponding alcohols and carbonyl compounds upon the irradiation in air of their solutions in acetonitrile in the presence of catalytic amounts of $HAuCl_4$ or in CH_2Cl_2 in the presence of $(C_4H_9)_4NAuCl_4$ [1]. In the present work, preliminary results are given for a study of the photocatalytic properties of cupric chloride in the oxidation of alkanes.

Irradiation of a solution of $5 \cdot 10^{-4}$ mole/liter anhydrous $CuCl_2$ and 0.46 mole/liter cyclohexane in acetonitrile in the air with visible light for 6 h leads to $1.70 \cdot 10^{-2}$ mole/liter cyclohexanol and $1.65 \cdot 10^{-2}$ mole/liter cyclohexanone. The product accumulation was linear and the reaction rate did not decrease after 6 h irradiation. The reaction rate at 4-60°C was virtually independent of temperature (effective $E_a < 15$ kJ/mole). Experiments on the oxidation of cyclohexane-d_{12} revealed a very slight kinetic isotope effect for this reaction $k_H/k_D = 1.2 \pm 0.2$. A low isotope effect (1.6) was also found when $FeCl_3 \cdot 6H_2O$ was used as the photocatalyst in analogous reactions.

Under analogous conditions, hexane was oxidized over 7.5 h to give $0.15 \cdot 10^{-2}$ mole/liter 1-hexanol, $0.28 \cdot 10^{-2}$ mole/liter 2-hexanol, $0.26 \cdot 10^{-2}$ mole/liter 3-hexanol, $0.39 \cdot 10^{-2}$ mole/liter hexanal, $0.64 \cdot 10^{-2}$ mole/liter 2-hexanone, and $0.66 \cdot 10^{-2}$ mole/liter 3-hexanone. The analogous reaction with ethylbenzene over 6 h gave $0.34 \cdot 10^{-2}$ mole/liter 1-phenylethanol and $1.1 \cdot 10^{-2}$ mole/liter acetophenone. The analogous reaction with styrene over 6 h gave almost exclusively $1.05 \cdot 10^{-2}$ mole/liter benzaldehyde. The combined competitive oxidation of ethyl

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benzene and cyclohexane showed that the reactivity of the CH_2 group in ethylbenzene relative to that of the analogous group in cyclohexane is 2.6. The corresponding reactivity is 1.7 in the reaction photocatalyzed by $FeCl_3$. The competitive oxidation method was used to show that the relative reactivity of the methyl group of substituted toluenes in the presence of $CuCl_2$ decreases in the series: $p\text{-}CH_3C_6H_4CH_3$ (3.1) > $CH_3C_6H_5$ (1.0) > $p\text{-}NO_2C_6H_4CH_3$ (0.1). Hence, we find $\rho^+ = -1.5$. This value coincides with the values for ρ^+ obtained for the photooxidation of the same substrates catalyzed by $FeCl_3$ and $AuCl_4^-$.

An $R^\cdot$ radical is presumably formed upon the reaction of photoexcited $CuCl_2$ [2] with an alkane molecule [3]. This radical reacts rapidly with O_2 to give $RO_2^\cdot$ radicals, which decompose, possibly with the participation of metal complexes to alcohol and ketone products. The Cu(I) derivative formed may be reoxidized either by oxygen or $RO_2^\cdot$ radicals.

EXPERIMENTAL

All the reactions were carried out in the air in a cylindrical glass vessel with a water jacket maintained at 15°C upon radiation with the full light of a 250-W DRL-250 (6) fluorescent lamp. The products were analyzed by gas-liquid chromatography on an LKhM-806 chromatograph on a 2-m column packed with 5% Carbowax 1500 on Inerton AW-HMDS with argon as the gas carrier and temperature programming at a rate of 4°C/min from 50 to 180°C.

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FREE RADICALS FORMED UPON THE REACTION OF SUBSTITUTED BENZOQUINONES WITH POTASSIUM AND ZINC BUTYLXANTHATES

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Potassium and zinc butylxanthates undergo one-electron transfer upon reaction with benzoquinones to give semiquinone radicals. The thiyl radical arising as a result of electron abstraction from the butylxanthate anion may add to the aromatic ring of the semiquinone radical.

Xanthates are now commonly used as reagents for the flotation enrichment of minerals. The attachment of the reagent on the mineral surface is presumably a consequence of electron density transfer from the reagent to the mineral [1]. In this case, charge transfer complexes and free radicals may be formed. However, under ordinary conditions, detection of free radicals formed as a result of the loss of an electron by the xanthate anion is impossible due to rapid recombination with the formation of a dixanthogenide.

$$ROC(S)S^- \xrightarrow[-e]{} ROC(S)S^\cdot$$

$$2ROC(S)S^\cdot \rightarrow ROC(S)SS(S)COR$$

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