PHOTOCHEMICAL REDUCTION OF POTASSIUM CHROMATE SOLUBILIZED WITH 18-CROWN-6 IN CHLOROFORM

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The cyclic polyether 18-crown-6 was used as a solubilizer to obtain a solution of potassium chromate in chloroform. While perfectly steady in darkness, the solution decomposes under the action of light. The decomposition reaction was monitored by measuring the decrease in the absorbance of chromate ions, and the rate constants, the temperature coefficient of the rate constant, and the quantum yield were determined. The mechanism of the reaction is discussed.

Chromate has been employed as oxidant for organic substrates in aqueous, nonaqueous, and mixed aqueous–nonaqueous systems[1–3]. Extraction of chromate ions from aqueous to nonaqueous solutions has been studied particularly in relation to the determination of Cr(VI), using quaternary ammonium bases[4], organometallic bases[5], and arsonium and phosphonium salts[6] as solubilizers. Extracted from acid aqueous solutions, the chromate ion is transferred into the organic phase as the B^+, $HCrO_4^-$ ion pair[6] (B^+ is the corresponding onium cation). Chromate ions are known[7] to be difficult to solubilize in organic solvents. No data are so far available concerning the kinetic stability of solutions containing a solubilized chromate or, if any, its redox reactions with the solvent.

Now, potassium chromate has been found easy to solubilize in chloroform by means of a cyclic polyether, 18-crown-6. Such solutions, however, are only steady in darkness; exposed to light they lose colour, which indicates that chromate reacts under such conditions. The aim of the present work was to examine this photochemical reaction, obtain the values of the kinetic parameters, and so to contribute to the understanding of the mechanism involved.

EXPERIMENTAL

18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was synthesized from triethyleneglycol and 1,8-dichloro-3,6-dioxaoctane[8]. The nonaqueous solution of potassium chromate was prepared by stirring a suspension of the crystalline reagent grade chemical (Lachema, Brno) in dry chloroform containing 18-crown-6 in a concentration of 50 mmol l^{-1}. The apparatus was protected against light. Prior to use, the solution was filtered and the concentration of chromate was determined spectrophotometrically. The stock solution was stored in darkness. The photochemical reaction was allowed to take place in a 220 ml glass vessel (Fig. 1) equipped with a glass stirrer. The solution was stirred constantly during the photochemical reaction applying a stirring speed of 900 rpm. The reaction vessel was fitted with a jacket thermostated to within $\pm 0{\cdot}1$°C and covered with asbestos, whereby the mixture was also protected from radiation other than that admitted through the window O. The light source was a HQE-40 mercury discharge tube (Berliner Glühlampenwerk, GDR), separated from the window by a thermal filter (T) and an optical filter (F) Hg MON 365. The thermal filter — a glass plate half blackened and half transparent — was horizontally movable. The reaction was triggered, after attaining a constant temperature inside the vessel and a constant performance of the discharge tube, by allowing the radiation to pass through the transparent part of the thermal filter. The stability of the luminous flux was checked by means of a Tesla 1PP75 photocell, which in the check experiments was interposed between the optical filter and the reaction vessel. The variations in the photocurrent measured over a period of 3 h did not exceed $\pm 4\%$ of the mean value recorded on a TZ 21S plotter (Laboratorní přístroje, Prague). Some of the experiments were performed on solutions from which oxygen had been removed with nitrogen (99·99 mol.% N_2), fed from a gas vessel through a polyethylene tube into the reaction vessel *via* the port N in its top part. Samples were taken in preselected time intervals by means of a tap K in the bottom of the vessel, and their absorbance was measured on a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena). The volume of the solution used was invariably 180 ml. The quantum yield was determined by means of a tris(oxalate)ferrate(III) actinometer[9]; the actinometer solution was made up by dissolving $K_3[Fe(C_2O_4)_3]\,.\,3\,H_2O$ in 0·5M-H_2SO_4. For the analysis of the reaction mixture, solutions of potassium iodide and silver nitrate were employed. The solution of KI was prepared by shaking an aqueous solution of the substance with chloroform containing 18-crown-6, passing the organic phase over a layer of anhydrous sodium sulphate, and filtering it. The solution of $AgNO_3$ was prepared by dissolving the chemical directly in chloroform containing 18-crown-6. Sodium chloride was solubilized likewise. Potassium chromate in the chloroform solution obeys the Lambert–Beer law, as tested at 27 300 cm^{-1} in the concentration region $c_{K_2CrO_4} = 25$ to

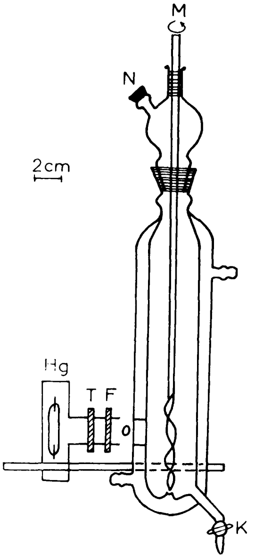

FIG. 1

Apparatus for conducting the photochemical reaction. Hg mercury discharge tube, T thermal filter, F optical filter, O window, N nitrogen inlet, M stirrer, K outlet tap

90 µmol l^{-1}. The rate constants were determined from the absorbance changes at 27 300 cm^{-1} by using the Guggenheim method for 1st order reactions[10]. The dependence log $\Delta A = f(t)$, where ΔA is the absorbance difference in times t and t', was invariably linear; the constant time interval $t - t'$ was longer than the reaction halflife, The relative error of the rate constant from three or four independent measurements did not exceed 6%.

RESULTS AND DISCUSSION

The absorption spectrum of chromate solubilized in chloroform ressembles that of chromate in neutral or weakly acid aqueous solutions (for aqueous systems see refs[11,12]). The spectral patterns are better resolved as compared with the aqueous systems, the maximum lies at 27 300 cm^{-1}, with marked shoulders at 28 180 and 26 100 cm^{-1} (Fig. 2, curve *1*). The molar absorptivity of chromate solubilized in chloroform also approaches that in aqueous solution, amounting to 4 800 l mol^{-1} cm^{-1} at 27 300 cm^{-1}. The solution is steady if stored in darkness; no spectral changes were observed in 48 h. On the other hand, rather rapid changes appear in the spectrum if the solution is exposed to ultraviolet radiation (Fig. 2, curves *1b*–*1d*). These changes are due to a chemical reaction, which in the reaction conditions applied is one of the 1st order. The rate constants at 293·1, 298·0, and 308·6 K are 4·5 . 10^{-4}, 5·0 . . 10^{-4}, and 6·0 . 10^{-4} s^{-1}, respectively. The same values, within the limits of experimental error,were measured for solutions from which atmospheric oxygen had been removed by purging with nitrogen for 30 min. The obtained plot of the logarithm of the experimental rate constant *vs* the reciprocal absolute temperature was linear, the temperature coefficient was 14·2 kJ mol^{-1}.

In the determination of the quantum yield the facts were taken into account that the incident radiation is absorbed incompletely in the reaction vessel and that the

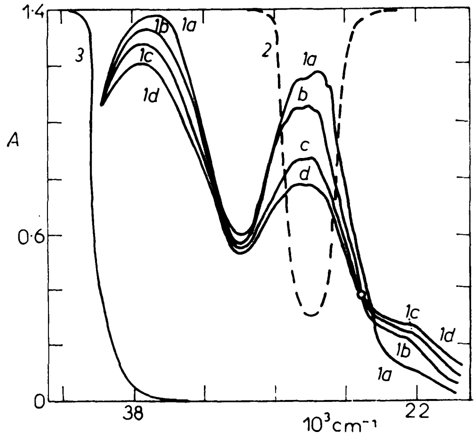

FIG. 2

Absorption spectra of chloroform solutions of solubilized potassium chromate, $c_{K_2CrO_4}$ = = 58 µmol l^{-1}, cell thickness 4 cm; *1a* unexposed sample, *1b* 20 min, *1c* 40 min, *1d* 60 min exposition. *2* spectrum of the optical filter, *3* spectrum of chloroform absorption by the reaction products is negligible as compared with the absorption by chromate. In such circumstances the quantum yield can be calculated[13] as

$$\varphi = (1/\bar{Q}_0 t)\,\{c_0 - c + (1/\varkappa_A d) \ln [(1 - \exp(-\varkappa_A c_0 d))/(1 - \exp(-\varkappa_A c d))]\}\,.$$

Here $\bar{Q}_0$ is the mean number of mole-quanta impinging on the reaction vessel in a unit time, t is the exposition time, c_0 is the intial concentration of the reactant and c is its concentration in time t, d is the thickness of the absorbing layer, and $\varkappa_A$ is the natural absorption coefficient (hence, $\varkappa_A = 2{\cdot}303a$, where a is the molar absorptivity). The $\bar{Q}_0$ value, determined for a thickness of 4 cm, was $1{\cdot}598 \,.\, 10^{-7}$ molquant s^{-1}. The quantum yield was measured 20, 30, and 60 min after the start of the reaction, and its mean value is $(2{\cdot}5 \pm 0{\cdot}6) \,.\, 10^{-2}$. A brown-gray precipitate, partly soluble in dilute hydrochloric acid, separated from the reaction system in several hours of irradiation, and chlorine and chloride ions were detected in the reaction mixture. After adding potassium iodide to the reacted solution, an intense absorption band was observed at 27 248 cm^{-1} due to the presence of I_3^- ions[14], which can arise from the reaction $I^- + I_2 = I_3^-$. The iodine required for this reaction stems from the iodide added, oxidized by chlorine formed as a reaction product. The chloride ions were detected by mixing the reacted chloroform solution of chromate with a chloroform solution of solubilized silver nitrate; a white turbidity appeared. (The reaction was previously checked with chloroform solutions of solubilized silver nitrate and solubilized sodium chloride.) In blank experiments performed with the unexposed chromate solution, no turbidity appeared even after several days storing of the system in darkness.

The time variations of the absorption spectrum of the chloroform solution of chromate give rise to an isosbestic point at 25 000 cm^{-1}, passed by all the traces except the first, corresponding to the unexposed sample ($t = 0$) (Fig. 2). This curve also shows a different position of the absorption maximum, shifted slightly towards lower wavenumbers against the remaining curves. A similar shift is apparent also for the short-wavelength absorption band. This reminds us of the shift that is observed in aqueous solutions due to the establishing equilibrium between CrO_4^{2-} and $HCrO_4^-$ ions[11,12,15]. According to[15], the equilibrium constant of the reaction $HCrO_4^- \rightleftarrows$ $\rightleftarrows H^+ + CrO_4^{2-}$ is $3{\cdot}7 \,.\, 10^{-7}$ at 25°C. Owing to the rather high value of molar absorptivity of the $HCrO_4^-$ ion (1 290 $l\,mol^{-1}\,cm^{-1}$ at 27 400 cm^{-1}), its effect on the absorption spectrum of chromate can be evaluated well also in neutral solutions, *i.e.*, at not very high concentrations of H^+ ions. The similarity between the absorption spectra of the chloroform solution of solubilized potassium chromate and of its aqueous solution warrants the interpretation of the spectral changes in terms of the reaction

$$CrO_4^{2-} + CHCl_3 \overset{h\nu}{\rightleftarrows} HCrO_4^- + CCl_3^- \qquad (A)$$

giving rise to a $HCrO_4^-$ ion and a trichlorocarbanion as a result of transition of the acidic hydrogen of chloroform to the CrO_4^{2-} ion. The $HCrO_4^-$ ion reacts with chloroform to give chromyl chloride and trichlorocarbanion, which is known[17] to decompose slowly to dichlorocarbene and a chloride anion. The presence of chromyl chloride as an intermediate is indicated by the increased absorption at 24 000 cm^{-1} (Fig. 2), where CrO_2Cl_2 is reported[16] to have a maximum. The other maximum of chromyl chloride, occurring[16] at 33 000 cm^{-1}, is apparently obscured by the absorption band of the $HCrO_4^-$ ion.

The above-mentioned decomposition of trichlorocarbanion gives rise to chloride ions, which actually have been detected in the reaction mixtur. The interpretation suggested is borne out also by the absorption spectrum of the solution of the soluble fraction of the brown-gray precipitate which can be observed to separate within several halflives of the reaction. The solution of this solid in 0·1M-HCl exhibits absorption maxima in the 17 000, 22 000, 28 000, and 46 000 cm^{-1} ranges, hence, near the positions of the absorption bands of hexaquachromium(III) and dichromate ions. Both ions can be formed from chromyl chloride adsorbed onto the solid product. Chromyl chloride is known[18] to decompose to dichromate, chromium trichloride, and chlorine in acid solutions.

Radical reactions are also conceivable, although their occurrence could not be proved by the method used. The $HCrO_4^-$ ion formed by virtue of reaction (*A*) is probably also photochemically active, which makes the interpretation of the reaction mechanism complicated. Since the changes in the absorption spectra and the observed rate constants are unaffected by oxygen (the spectral patterns for solutions which had or had not been purged with nitrogen were identical), oxidation of chloroform by atmospheric oxygen under the action of light, giving rise to carbonyl chloride and hydrogen chloride[19], obviously does not participate. Of interest is also the high sensitivity to light of the chloroform solutions of potassium chromate solubilized with the cyclic polyether 18-crown-6, where apparent spectral changes occur even under the action of diffuse daylight, as observed in preliminary experiments; this contrasts with the virtually unlimited stability in darkness.

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