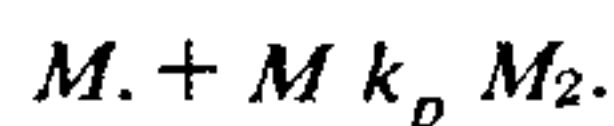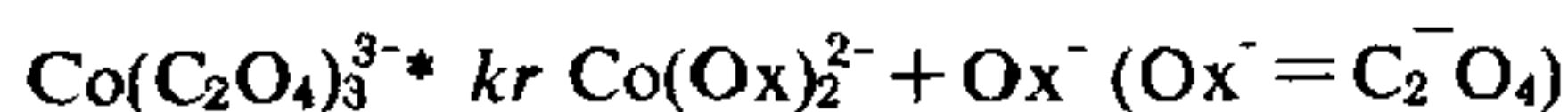trend as shown in figure 1, Plot B. (7.) The dependence of $-d[M]/dt$ on $[I]^{0.33}$ may be due to practical limitations. Hsiachen[11] observed a light intensity dependence of 0.4, in the study of photopolymerization of acrylamide in *ethylene glycol* sensitized by thiazine dyes with triethanolamine. (8.) $-d[C]/dt$ was directly proportional to the first power of $[C]$ and $[I]$.
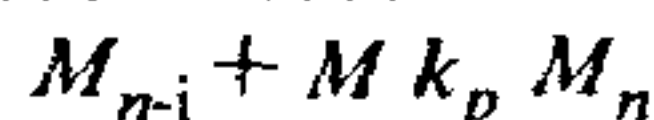
The following reaction scheme prima facie may account for the experimental observation.

$$Co(C_2O_4)_3^{3-} \xrightarrow[k_\epsilon I]{h\nu} Co(C_2O_4)_3^{3-*}$$

$$[C] \xrightarrow[k_d]{} [C]^*$$
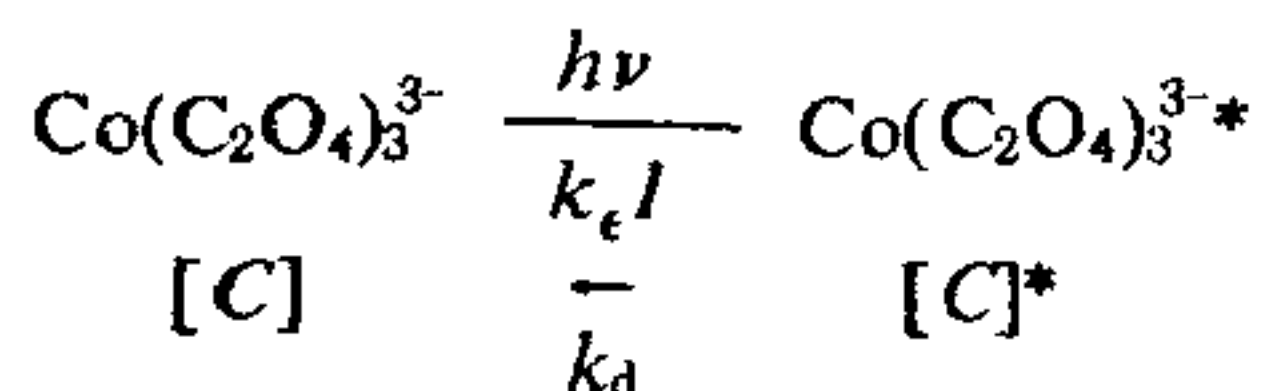
$Co(C_2O_4)_3^{3-*}$ was the excited complex and k_d, the rate constant for the dark back reaction of the excited complex.

$$Co(C_2O_4)_3^{3-*} \xrightarrow{kr} Co(Ox)_2^{2-} + Ox^- \quad (Ox^- = C_2^- O_4)$$

$$Co(C_2O_4)_3^{3-} + Ox^- \xrightarrow{k_s} Co^{2+} + 3\ Ox^{2-} + 2\ CO_2$$

$$Ox- + M \xrightarrow{k_i} M.$$

$$M. + M \xrightarrow{k_p} M_2.$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$M_{n-i} + M \xrightarrow{k_p} M_n$$

$$M_n + M_m \xrightarrow{k_t} M_{n\cdot m}$$

Assuming the steady state conditions for free radicals, the following rate expressions are derived.

$$d[M]/dt = \frac{k_p}{k_t^{1/2}} \left[\frac{k_r k_\epsilon I}{k_r + k_d} \right]^{1/2} [M]$$

$$-d[C]/dt = \frac{k_r}{k_r + k_d}[C]I$$

We have noticed that the rate of monomer disappearance, $-d[M]/dt$ and the rate of complex disappearnace, $-d[C]/dt$ increased with increasing hydrogen ion concentration. This might be explained by considering protonation of one of the oxalato ligands in $Co(Ox)_3^{3-}$ followed by the production of hydrogen atoms in acidic solutions[12].
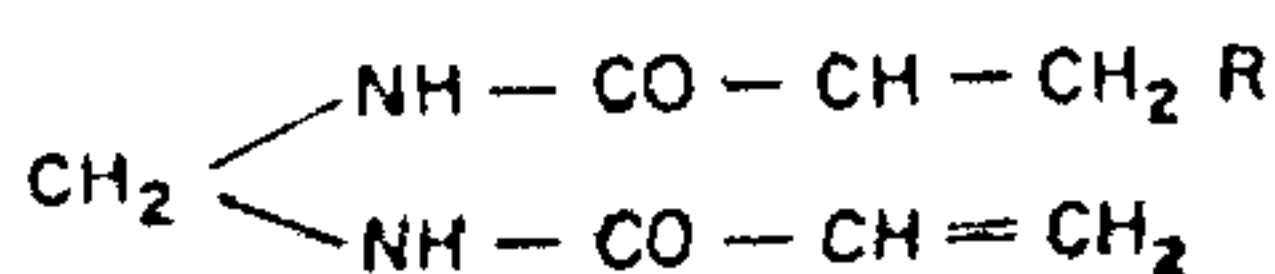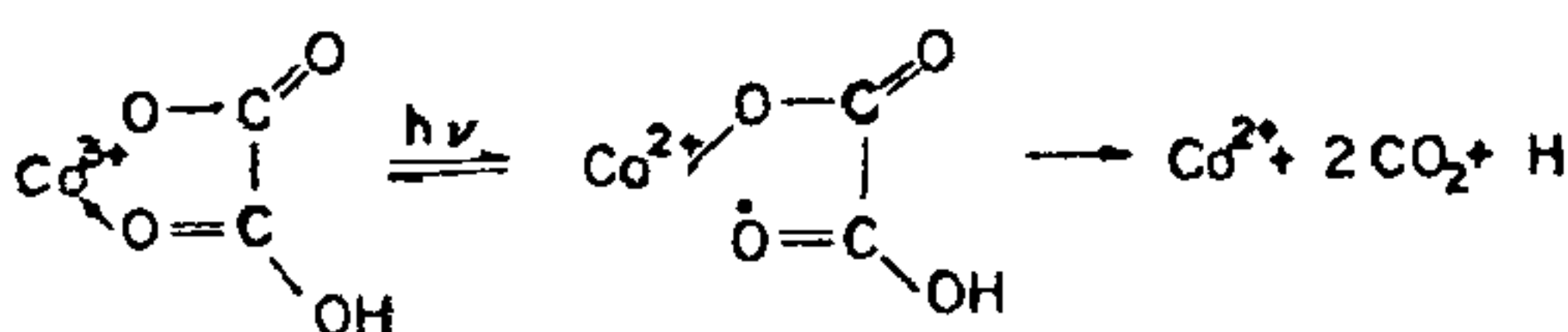
These hydrogen atoms account for the increased rate of polymerization. Our observations in this regard coincide with that of Shaik Mahaboob *et al*[7].

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AN IMPROVED SYNTHESIS OF CHALCONES USING TRIETHYL BENZYL AMMONIUM CHLORIDE (TEBA)

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BASE catalysed condensation[1] of appropriate acetophenones and benzaldehydes in aqueous ethanolic medium has been most commonly adopted for obtaining chalcones of desired substitution patterns, though there are other methods available for their preparation[2], largely because of the simplicity of this method and ready accessibility of starting materials with a wide variety of substitution patterns. Benzaldehydes are normally taken in slight excess, to make up for their consumption by the accompanying Cannizzaro reaction, during the course of condensation.

TABLE 1

Chalcones: 3–16.

Product No.	R^1	R^2	R^3	R^4	R^5	R^6	% Yield without TEBA	% Yield using TEBA	Observed m.p. °C	Literature m.p. °C
3	H	H	H	H	H	H	25	71	89–90	89–90[7]
4	H	H	H	H	OCH₃	H	25	64	93–94	95[8]
5	H	H	H	H	OCH₃	OCH₃	27	66	115	114–115[9]
6	H	OCH₃	H	H	H	H	25	80	104–105	105[10]
7	H	OCH₃	H	H	OCH₃	H	35	74	113–114	113–114[20]
8	H	OCH₃	H	H	OCH₃	OCH₃	28	78	155–156	156[11]
9	H	H	OCH₃	H	OCH₃	H	37	83	130–131	130[12]
10	H	H	OCH₃	H	OCH₃	OCH₃	41	72	117–118	118[13]
11	OCH₃	OCH₃	H	H	H	H	27	93	97–98	98[14]
12	OCH₃	OCH₃	H	H	OCH₃	H	25	86	129–131	131–132[15]
13	OCH₃	OCH₃	H	H	OCH₃	OCH₃	25	92	123–124	124–125[16]
14	H	OCH₃	H	OCH₃	H	H	35	86	90–91	90–91[17]
15	H	OCH₃	H	OCH₃	OCH₃	H	37	85	109–110	111–112[18]
16	H	OCH₃	H	OCH₃	OCH₃	OCH₃	25	80	152–153	151[19]

Acidification of the diluted reaction mixture after stipulated time (8–48 hr) with hydrochloric acid gives a mixture of the expected chalcone and aromatic carboxylic acid with unreacted aldehyde sticking to it. This necessitates a step of fractional crystallisation from appropriate solvent resulting in unsatisfactory yields, of the required product[1]. We had prepared several chalcones by this method for reduction to the corresponding dihydrochalcones and subsequent reaction with diiodomethane[3] and we had observed similar difficulty in getting satisfactory yields of chalcones.

Quaternary ammonium salts have found extensive application in increasing the efficiency of organic reactions in liquid-liquid and liquid-solid two phase systems involving carbanion intermediates[4]. The use of tetra-*n*-butyl ammonium iodide in the synthesis of isoflavanones[5] and tetra-*n*-butyl ammonium hydrogen sulphate in a facile Baker-Venkataraman synthesis of flavones[6] has recently been reported from our laboratories.

The condensation between acetophenones and benzaldehydes when carried out in two phase system using either benzene or dichloromethane and aqueous potassium hydroxide (10%) or saturated solution of potassium carbonate in the presence of triethyl benzyl ammonium chloride or tetra-*n*-butyl ammonium iodide did not proceed effectively. Even after 48 hr of vigorous stirring, unreacted acetophenone and benzaldehyde were the major components of the reaction mixture (TLC).

It has now been observed that condensation of various acetophenones and aromatic aldehydes in aqueous ethanolic medium containing potassium hydroxide proceeds extremely satisfactorily in the presence of triethyl benzyl ammonium chloride. Tetra-*n*-butyl ammonium iodide and tetra-*n*-butyl ammonium hydrogen sulphate did not prove as efficient. The yields of chalcones have been found to be better when aromatic aldehyde is used in large excess (~1.5 molar ratio). Conventional method of working up mentioned above has been modified. Sulphur dioxide when passed through the reaction mixture, after the condensation has progressed to completion, converts unreacted aldehyde into its soluble bisulphate addition product and precipitates out the desired chalcone and aromatic acid. This mixture on treatment with aqueous sodium bicarbonate gives chalcone in a pure state, homogeneous on TLC, having the recorded m.p. The scope of this method consists of studying the condensation of a number of acetophenones and benzaldehydes as detailed in the table. The desired chalcones have been obtained in 64–93% yield.

Parallel set of experiments without the use of triethyl benzyl ammonium chloride gave these chalcones in poor yields (25–41%). The use of a large excess of benzaldehyde and the modified procedure of working up with sulphur dioxide did not improve the yields in this case.

Quaternary ammonium salt appears to provide a convenient cation for the counter ion (carbanion) generated during the course of chalcone condensation and helps it to progress in the desired direction. It is an interesting example of catalysis by a quaternary ammonium salt in a homogeneous phase.

General Procedure

Substituted acetophenone (1 mole), appropriate benzaldehyde (1.5 mole), triethyl benzyl ammonium chloride (1 mole) and aqueous potassium hydroxide (30%) were taken in ethanol so as to give an overall 10% concentration of alkali in a homogeneous medium. After 24 hr of stirring at 30°, the reaction mixture was cooled to 0° and a steady stream of sulphur dioxide was passed through it. The solid that separated was filtered and treated with cold aqueous sodium bicarbonate until there was no more effervescence. Chalcone thus left behind was filtered and crystallised from ethanol/dilute ethanol.

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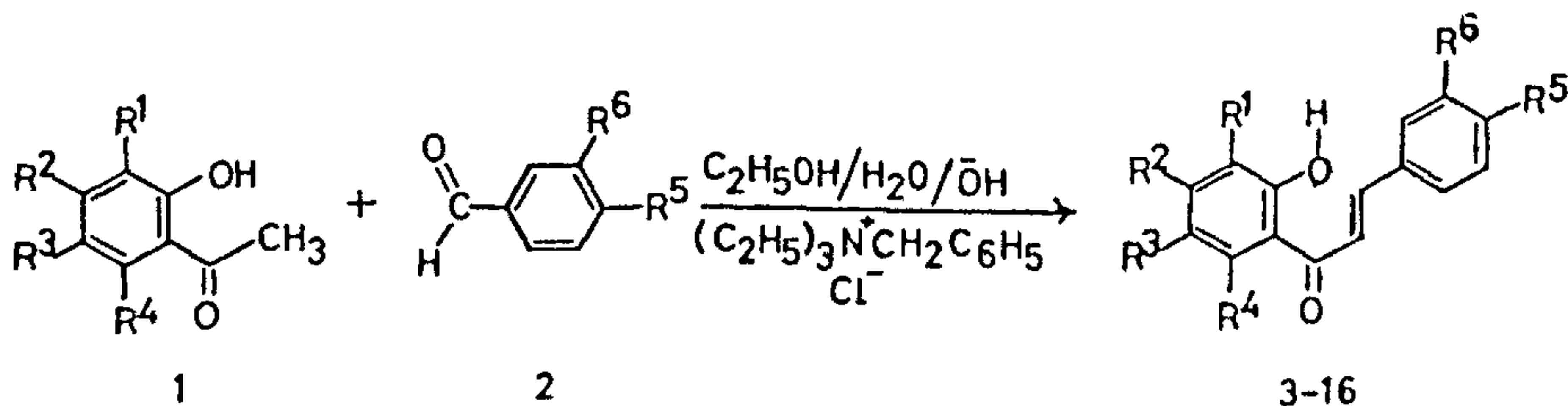
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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM AS MOLYBDOARSENO-ZIRCONIC ACID

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SPECTROPHOTOMETRIC methods for the estimation of zirconium based on heteropolyacid formation have been described. Dehne and Mellon[1] utilised the reaction of zirconium with molybdate and sulphate to form the ternary heteropolyacids for the determination of zirconium after reduction to the heteropoly blue. Murata *et al*[2] have developed a method for zirconium based on the formation of molybdophosphozirconic acid. In this method, because of the very high absorbance of molybdophosphoric acid formed under the experimental conditions, prior extraction of the binary heteropoly acid into butylacetate is necessary before subjecting the aqueous phase for absorbance measurements. In the course of our investigations, it was found that replacement of phosphorus by the arsenic in the ternary system can render the method simple, as the molybdoarsenic acid formed if any, did not interfere with the determination of zirconium as molybdoarsenozirconic acid, and therefore eliminated the prior separation step. The details of investigations that led to the development of such a procedure are furnished in this communication.

Apparatus: All spectrophotometric measurements were made by using Carl-Zeiss spectrophotometer with 1 cm quartz cells. A Knick pH meter was used for measuring the pH. Analytical grade chemicals were used. Zirconium, 100 ppm—Suitable amounts of $ZrOCl_2 . 8H_2O$ dissolved in 1:1 hot sulphuric acid and the solution suitably diluted. Ammonium molybdate solution 0.05 M and sodium arsenate solution, 0.01 M were prepared by standard methods.

Procedure: Transfer an aliquot containing not more than 1000 μg of zirconium into a 100 ml beaker. Add 5 ml of ammonium molybdate and 2.5 ml of sodium arsenate and dilute to 50 ml. Adjust the pH of the solution to 1.5 using dilute sulphuric acid and ammonium hydroxide and heat the solution on a boiling water bath for about 20 min. Allow the solution to cool to room temperature and make up to 100 ml with distilled water. Measure the absorbance of the solution using 10 mm quartz cell at 340 nm, using blank as reference and establish the concentration by reference to a calibration graph prepared for 100 to 1000 μg following the above procedure.

Preliminary absorption spectra of the sample against the reagent blank showed that molybdoarsenozirconic acid absorb maximally at 323 nm. As the blank also absorbed considerably at this wavelength, it was decided to make measurements at 340 nm where the blank absorption was less. The absorbance remained constant in pH range 1.3-2.3 and therefore all further studies were made at 1.5.

The effect of ammonium molybdate and sodium arsenate concentration showed a constant and maximum absorbance when the aqueous phase contained at least 5 ml of 0.05M ammonium molybdate and 2.5 ml of 0.01M sodium arsenate. It was found that an optimum time of 20 min of heating over a boiling water bath was enough for maximum colour development. The system with a molar absorptivity of 7.63×10^3 1 mole^{-1} cm^{-1} obeyed Beer's law upto 10 ppm of zirconium. The Sandell sensitivity was calculated to be 0.012μg cm^{-2} when measurements were made at 340 nm.

The combining ratios of molybdenum, arsenic and