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ALLYLIC OXIDATION OF (+)-CAR-3-ENE

THE oxidation of (+)-car-3-ene (I) by oxidising agents like potassium permanganate[1] in acetone, chromic acid[2] in acetone and pyridine, has been reported to give a complex mixture of compounds consisting of acids and neutral compounds. In these methods the neutral oxidation products were obtained in about 10–15% yield and have been separated into their constituents by employing column chromatography, fractionation and preparative GLC techniques.

In our attempts to convert (I) into *cis* caronic acid (II), we were interested in a suitable method of converting (I) into the intermediate diketone (III), so that the latter could be oxidised to (II) by the known procedure[3]. The formation of (III) has been reported only in the oxidation of (I) by potassium permanganate[1].

With a view to obtaining the diketone (III), (I) was subjected to allylic oxidation using sodium dichromate-acetic acid[4] (48 hrs, at room temperature, 1·5 moles of $Na_2Cr_2O_7$) to give the oxidation product, which was chromatographed on alumina (Gr. II, 1:20) and eluted with pet. ether, pet. ether + benzene (1:1), benzene, chloroform and acetone. The fraction eluted with pet. ether (70% of the total oxidation product) chiefly consists of unchanged (I) along with rearranged hydrocarbons, according to IR spectrum and comparative GLC.

The fraction eluted with pet. ether-benzene (TLC. 5-spots) being in small quantity was not investigated. Some of the fractions eluted with benzene gave a liquid ketone (TLC, 1 spot, 95% pure by GLC) which was further purified by distillation [b.p. 140–145° (bath)/4 mm] and identified as 1,1,4-trimethyl, 2,4-diene-6-one (IV) as per elemental analysis and spec-

tral data; $C_{10}H_{14}O$, M^+ 150, IR bands: 1650 ($\geq C = O$ of completely conjugated dienone); 1610 (conj –HC=CH– and $\geq C=CH$), 1,380, 1,365 cm^{-1} (gem dimethyl); NMR (CCl$_4$) signals at τ: 8·92 (6H, s, gem dimethyl at C_1); 8·0 (3H, s, C_4-vinyl CH$_3$); 7·5 (2H, s, C_7–CH$_2$ adjacent to $\geq C=O$); 3·95 (1H, d, J = 13·2 Hz, C_2-olefinic proton); 4·32 (1H, d, J = 13·2 Hz, C_3-olefinic proton) and 4·10 (1H, s, olefinic proton at C_5); UV λ_{max} 298 mμ, ε_{max} 5500;

I   II   III

IV   V   VI
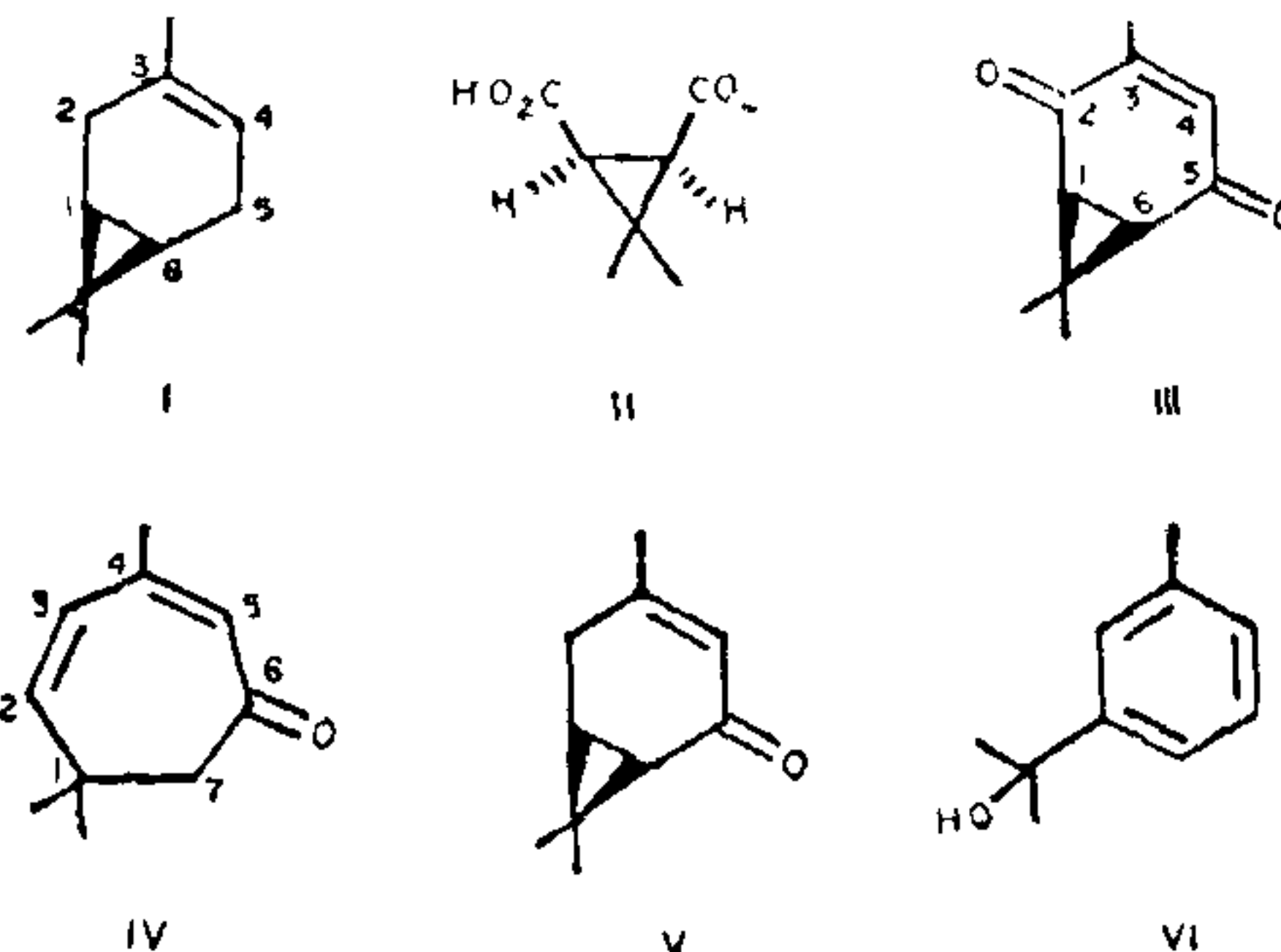
2:4 DNP $C_{16}H_{18}O_4N_4$, m.p. 173–175° (Lit.[2] records for 2:4 DNP of IV, m.p. 175–176°). As reported[2] earlier, ketone (IV) might have been formed by acid rearrangement of the ketone (V), also expected to be formed from (I) in the reaction. The tail fractions eluted with benzene (TLC, single spot) on crystallisation from ethanol gave a solid, $C_{10}H_{12}O_2$ m.p. 95–96°, identified as car-3-ene 2, 5-dione (III) by physical constants and spectral data. IR bands at 1650 (conj. $\geq C=O$), 1613, 858 cm^{-1} (conj. –CH=C ζ); NMR (CCl$_4$) signals at τ: 8·63, 8·67 (6H, s, gem dimethyl on cyclopropane); 8·07 (3H, s, C_3-vinyl CH$_3$); 7·8 (2H, s, cyclopropyl protons at C_1 and C_6) and at 3·6 (1H, br S, olefinic proton at C_4); UV λ_{max} 227 mμ, ε_{max} 8800; 241 mμ, ε_{max} 10420; dioxime $C_{10}H_{14}O_2N_2$, m.p. 182–3° (Lit.[3] records for dioxime of III, m.p. 185°).

The fractions eluted with chloroform were purified by chromatography over alumina and the tail fractions distilled to give a liquid alcohol $C_{10}H_{14}O$, M^+ 150 identified as *m*-cymenol (VI) by spectral data: IR bands 3400 (OH), 4 bands at 1961, 1887, 1792, 1754 (all weak bands) (meta disubstituted benzene), 1605, 1587 cm^{-1} (aromatic); NMR (CCl$_4$) signals at τ: 8·5 (6H, s, methyls of hydroxy isopropyl); 7·65 (3H, s, CH$_3$-aromatic); 7·27 (s, 1H, exchangeable with D$_2$O, OH-proton); 3·04 and 2·67 (4H, m, aromatic protons).

The major oxidation product was found to be *m*-cymenol (VI) while ketones (III) and (IV) were obtained in about 2·5% yield each.

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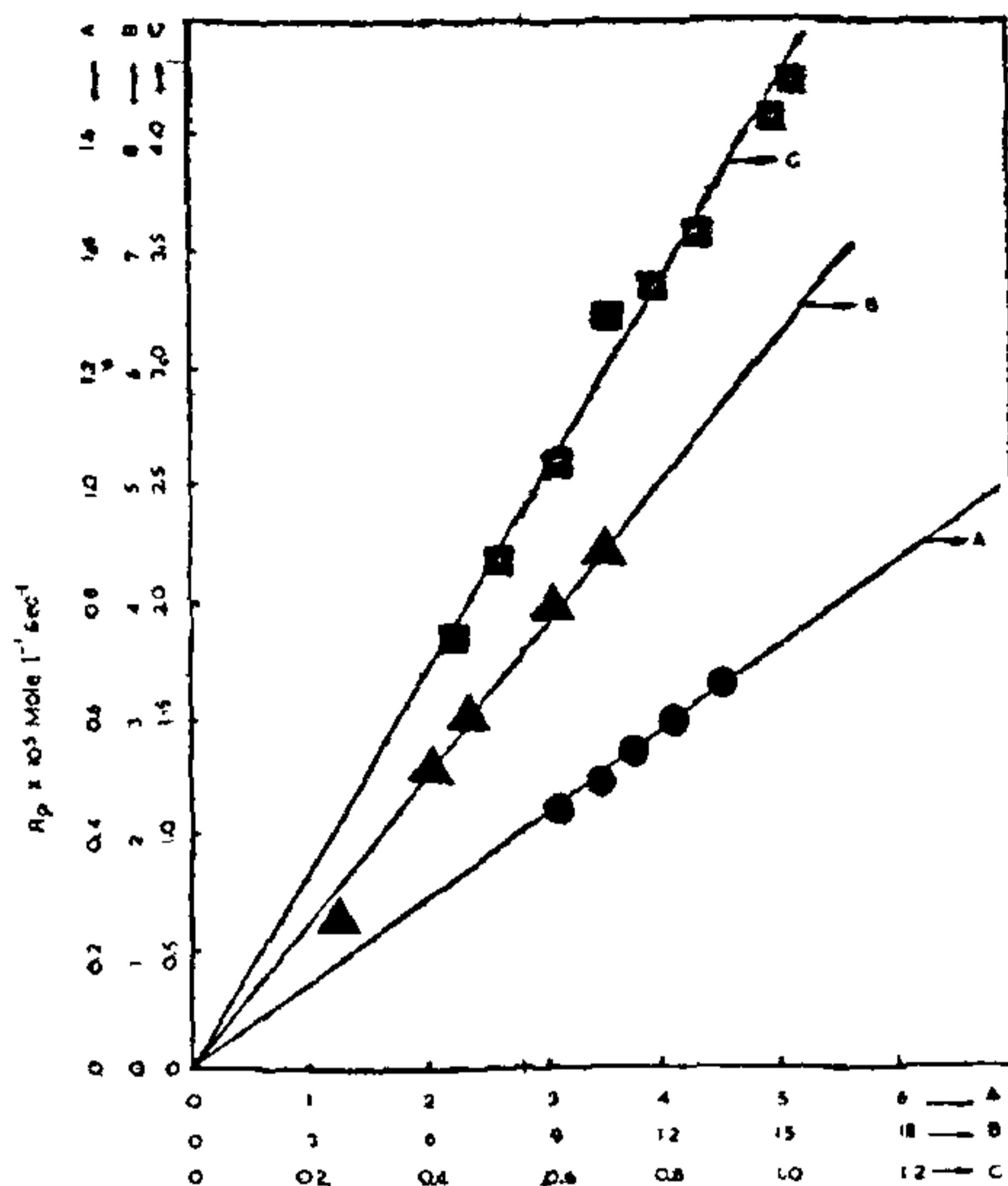B. M. MANE.
R. S. JOSHI.
G. H. KULKARNI.

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CERIUM(IV)-BENZYL ALCOHOL REDOX SYSTEM FOR ACRYLONITRILE POLYMERIZATION

NUMEROUS reducing agents like alcohols[1], aldehydes[2,3] acids[4] have been used in combination with Ce(IV) for aqueou vinyl polymerization. In all these systems, the primary initiation species is the radical produced from the substrate by oxidation with Ce(IV). Literature survey on vinyl polymerization reveals that benzyl alcohol has not been used as a reducing agent in combination with Ce(IV) for vinyl polymerization. The oxidation[5-7] of benzyl alcohol by Ce (IV) has been shown to proceed through the formation of intermediate radical $C_6H_5CH_2O\cdot$ which subsequently decomposes to give the product benzaldehyde. In this communication we report the studies on thermal polymerization of acrylonitrile (AN) at 20° C in nitric acid medium by the redox system Ce(IV)-benzyl alcohol (BA).

The polymerization experiments were conducted in the dark under deaerated conditions at constant pH (pH = 1·7) and ionic strength, $\mu = 0\cdot2$ M. The [ANt] was varied from 0·45 to 1·05 M [Ce(IV)] from 1×10^{-4} to 1×10^{-3} M, [BA] from 2×10^{-4} to 2×10^{-3} M. The rate of polymerization was followed gravimetrically and that of Ce(IV) disappearance by titrimetry.

The following are some of the salient features of the polymerization reaction. The steady state was attained in about 15 minutes. The rate of polymerization (R_p) was directly proportional to [AN] and to the square roots of [Ce(IV)] and [BA] (Fig. 1). The first order dependence of R_p on [AN] observed here, is a rare occurrence since orders 1·5 and 2 were reported for Ce(IV) initiated vinyl polymerization reactions[1-4]. $-R_{Ce(IV)}$, namely the rate of Ce(IV) disappearance, was individually proportional to first powers of [Ce(IV)] and [BA]. There was no polymerization in
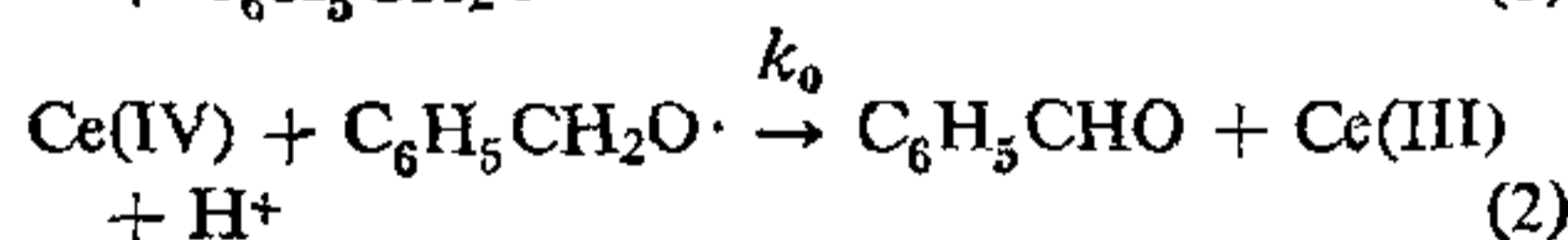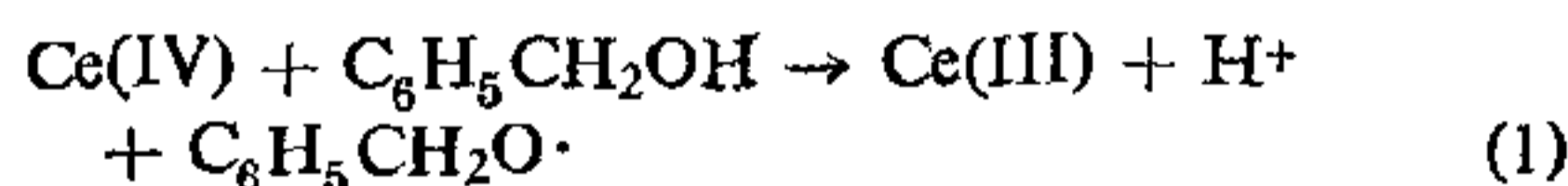

FIG. 1. Plots of rates of polymerization against (A) square root of benzyl alcohol concentration. (B) square root of ceric ion concentration, (C) acrylonitrile concentration.

$A = [BA]^{0.5}$ (Mole. $l^{-1})^{0.5} \times 10^2$; $B = [Ce(IV)]^{0.5}$ (Mole. $l^{-1})^{0.5} \times 10^2$; $C = [AN]$ (Mole. l^{-1})

the absence of benzyl alcohol under the present experimental conditions.

Our results lead to the following conclusions. :
1. Under the present experimental conditions, namely 20° C, oxidation of water by Ce(IV) producing OH· and the initiation of vinyl polymerzation by Ce(IV) do not occur. 2. The reaction Ce(VI) + benzyl alcohol produces the free radical $C_6H_5CH_2O\cdot$ which may partly be oxidised by Ce(IV) to give the products (eqn. 2).

$$Ce(IV) + C_6H_5CH_2OH \rightarrow Ce(III) + H^+ + C_6H_5CH_2O\cdot \tag{1}$$

$$Ce(IV) + C_6H_5CH_2O\cdot \xrightarrow{k_0} C_6H_5CHO + Ce(III) + H^+ \tag{2}$$

and partly reacts with the monomer initiating polymerization.

$$C_6H_5CH_2O\cdot + M \xrightarrow{k_i} M\cdot \tag{3}$$
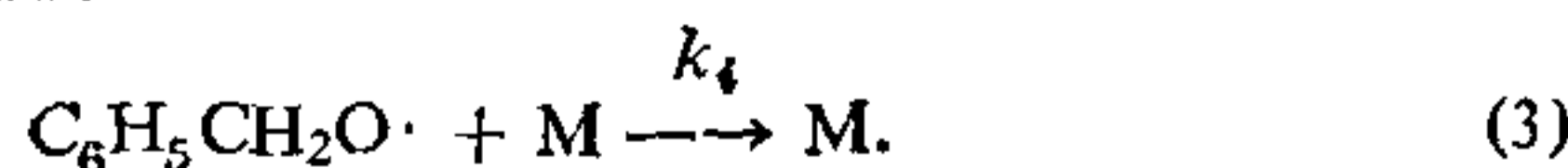
This is followed by the usual propgation steps.

$$M\cdot + M \xrightarrow{k_p} M_2\cdot \tag{4}$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot \text{ etc.} \tag{5}$$