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DICUMYLBARIUM. A NOVEL INITIATOR IN ANIONIC POLYMERIZATION. ITS PHYSICOCHEMICAL PROPERTIES IN TETRAHYDROFURAN AND TETRAHYDROPYRAN

LEONG CHAI TANG, CLAUDE MATHIS and BERNARD FRANCOIS
Centre de Recherches sur les Macromolécules (CNRS) 6, rue Boussingault - 67083 Strasbourg Cedex (France)

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Summary

The preparation of dicumylbarium by reaction of methyl cumyl ether with finely-divided barium in tetrahydrofuran (THF) and tetrahydropyran (THP) is described. The salt was characterized by spectrophotometric and chemical methods. Conductance studies for 10^{-3} to 10^{-5} M concentrations of the salt in THF at temperatures from 15 to −70°C and in THP from 15 to −30°C demonstrated the presence of triple ions in thermodynamic equilibrium with free ions and ion pairs. In THF the dissociation constant varies from 1.0×10^{-9} M at 15°C to 2.3×10^{-9} M at −70°C, the corresponding enthalpy and entropy of reaction being −1.1 kcal mol^{-1} and −45 e.u. respectively. In THP, however, dissociation of the salt is too weak to be determined directly. Kinetic studies of the protonation reaction between dicumylbarium and triphenylmethane in THF showed that the apparent rate of reaction is 1.65×10^{-5} sec^{-1}, independent of carbanion concentration. This indicates that protonation proceeds exclusively via free ions and hence provides further evidence for the presence of triple ions in dicumylbarium solutions.

Introduction

Many accounts have appeared on the anionic polymerization of unsaturated compounds by alkali metals and their organic derivatives [1]. While some of these initiators such as cumylpotassium and organolithium salts lead to the formation of monocarbanionic living polymers, others such as sodium naphthalene and the tetramers of α-methylstyrene give bicarbanionic living polymers.

Exception for studies involving magnesium and its organic derivatives, only until recently little work had been done on the use of alkaline-earth metals and their compounds in anionic polymerization [2–12]. Use of these metals as initiators has been reported to give rise to difficulties. The mechanism of polymerization was complex and could only be explained on the basis of a simultaneous participation of

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ionic species and free radicals [13]. The organic derivatives of alkaline-earth metals are more difficult to synthesize than those of the alkali metals, and the monofunctional derivatives of these metals so far employed as initiators, are either relatively inefficient, e.g. bis(triphenylmethyl)- and di(4-fluorenyl)barium, or not well-defined, e.g. oligo-α methylstyrylbarium.

In this paper, we describe the preparation and characterization of a novel initiator, namely dicumylbarium and [bis(phenyldimethylcarbinyl)barium]. Among alkaline-earth metal compounds, this is the first well-defined and highly efficient monofunctional initiator. To investigate this salt in solution, we have carried out spectrophotometric and conductance studies on its solutions in THF and THP (tetrahydropyran). The kinetics of its reaction with triphenylmethane in THF have also been studied in an attempt to determine the reactivities of the ionic species present.

Experimental

THF and THP were purified by the usual procedures. Details on the conversion of commercially available barium into a finely-divided powder have been given elsewhere [14,15].

The synthesis of dicumylbarium involves two steps:

(1) Preparation of methyl cumyl ether. This was made by Ziegler's method [16]. The ether was purified by fractionation under reduced pressure on a spinning band column, the purities of the various fractions being checked by use of an Intersmat Gas Chromatograph. The procedure was repeated until the impurities, mainly residual α-methylstyrene, were reduced to about 0.02%. The ether was then distilled through a high-vacuum line on to sodium wire for further drying, and subsequently redistilled into small ampoules and sealed off for cold storage.

(2) Reaction of methyl cumyl ether with barium. This reaction was carried out in an evacuated all-glass apparatus equipped with a sintered filter and an optical quartz cell. An excess of barium was dispersed into 100 cm^3 of a THF or THP solution of methyl cumyl ether (ca. 4×10^{-3} M) at below -60°C. The mixture was stirred at room temperature for nearly two days.

All optical spectra were recorded on a Beckman Acta V UV/visible spectrophotometer. The sample compartment of the spectrophotometer was equipped with a specially designed thermostat unit which enables the temperature to be varied from 20 to -105°C.

Conductance studies were performed under high vacuum in all-glass apparatus containing a conductance cell and an optical quartz cell. Before the measurements the internal walls of the apparatus were thoroughly purged with a carbanionic solution of the salt and then rinsed carefully with the solvent distilled from this solution by external cooling. Conductivities were measured with the aid of a Wayne Kerr Universal Bridge operating at 1592 cycles per second for a series of concentrations from 10^{-3} to 10^{-5} M and for each concentration over the entire temperature range from 15 down to -70°C at about 10° intervals. Since THP freezes at -45°C, the conductivities of the salt in this solvent were measured only from 15 to -30°C. The concentration was varied by the usual internal dilution technique [17].

The proton-transfer reaction was studied at 15°C in THF. Triphenylmethane was dried under vacuum. After measurement of the concentration of the dicumylbarium solution, a small quantity of the solvent was distilled onto the protonating agent to dissolve it and then the reagents were rapidly mixed. The progress of the reaction was followed spectrophotometrically by monitoring the absorption of the triphenylmethyl carbanion at its maximum of 462 nm. The procedure was repeated for different concentrations.

Results and discussion

Formation of carbanion

In THF the optical spectrum of dicumylbarium exhibits a maximum absorption at 338 nm. The formation of the carbanion as measured spectrophotometrically at this wavelength in the course of preparation is depicted in Fig. 1. The result shows that maximum conversion was obtained after 48 h. The time-dependence of the logarithmic increase of this absorption is linear up to about 94% conversion, indicating that the reaction is first order with respect to the concentration of metal involved.

Methyl cumyl ether is known to decompose easily into α-methylstyrene and methanol even when kept in vacuum at low temperature. Such a decomposition would result in a bicarbanionic oligomer of α-methylstyrene. To confirm the presence of the cumyl carbanion, the salt prepared was treated with water, methyl iodide, n-butyl bromide and 1,1-diphenylethylene respectively. The products were analyzed by gas chromatography using as references the compounds derived analogously from cumylpotassium, and were identified as cumene, 2-methyl-2-phenylpro-

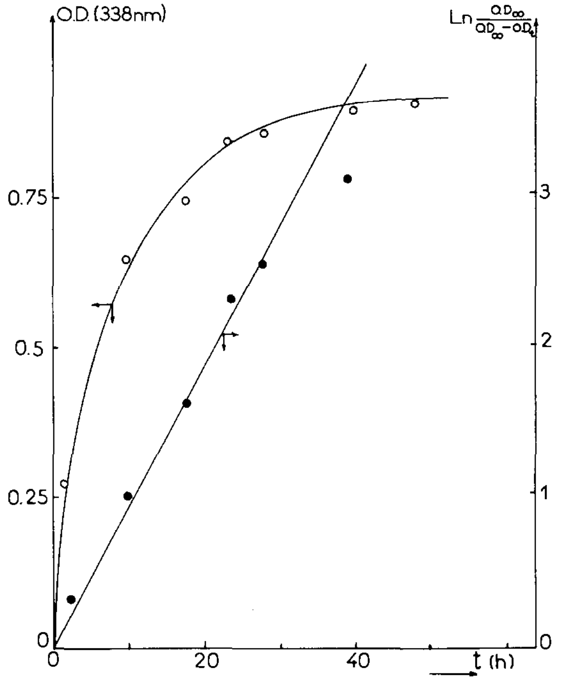
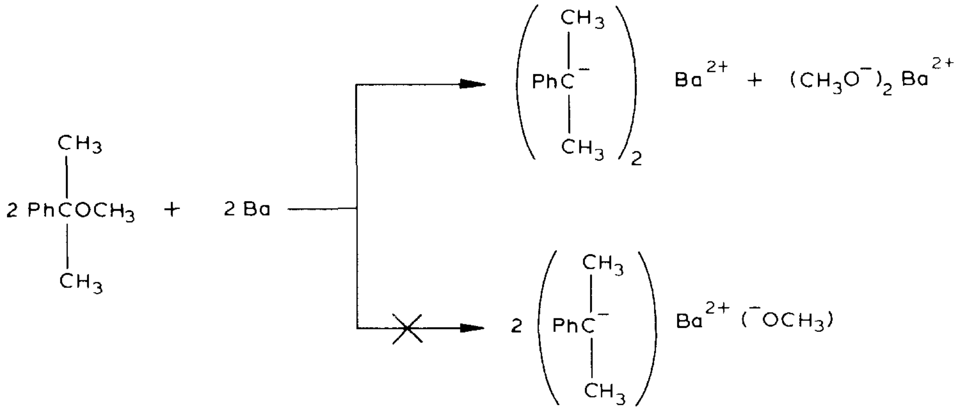


Fig. 1. Kinetics of the formation of dicumylbarium in THF.

pane, 2-methyl-2-phenylhexane and 1,1,3-triphenyl-3-methylbutane, respectively. The reaction between methyl cumyl ether and barium thus yields a cumyl salt and a methoxide in stoichiometric quantities. Barium methoxide is insoluble in THF and was separated from the carbanionic after filtration. When the solution was deactivated with water and analyzed by gas chromatography, no trace of methanol was detected, which rules out the formation of a mixed species designated by 1 in the following scheme:



(I)

Spectral studies

The maximum absorptions of dicumylbarium in THF (λ_{max} 338 nm) and in THP (λ_{max} 335 nm) are close to those for the corresponding potassium and cesium salts [17,18]. The λ_{max} is independent of the carbanion concentration in THF and remains practically unchanged at low temperature (Fig. 2). However, a gradual diminution of this absorption, was observed on prolonged storage at room temperature due to loss of the carbanion (Fig. 3) but the solutions are stable for months at −30°C.

Reaction of a minute quantity of styrene with dicumylbarium gives oligostyrylbarium. For a degree of polymerization corresponding to the addition of an average of 1.5 monomer unit per cumyl carbanion, the λ_{max} was displaced from 338 to 360 nm. This value does not depend on degree of polymerization and is in good agreement with that previously found for the monocarbanionic polystyryl salt [8]. On the other hand, we have also shown that the λ_{max} of oligomeric α,ω-bicarbanionic polystyrylbarium varies considerably with its degree of polymerization. These results therefore confirm that the variation is related to the bicarbanionic nature of the living polymer and the interaction between chain ends rather than to any direct influence of the penultimate or antipenultimate monomer units.

When dicumylbarium was treated with 1,1-diphenylethylene, a new peak was seen at 456 nm. This λ_{max} is different from the reported 450 nm for the corresponding bicarbanionic salt [15].

The extinction coefficient of the cumyl salt was found to be 12,000 (which compares with values of 18,000 for bis(1,1-diphenylethyl)barium and 12,000 for polystyrylbarium.) The value was confirmed by titration with catechol.

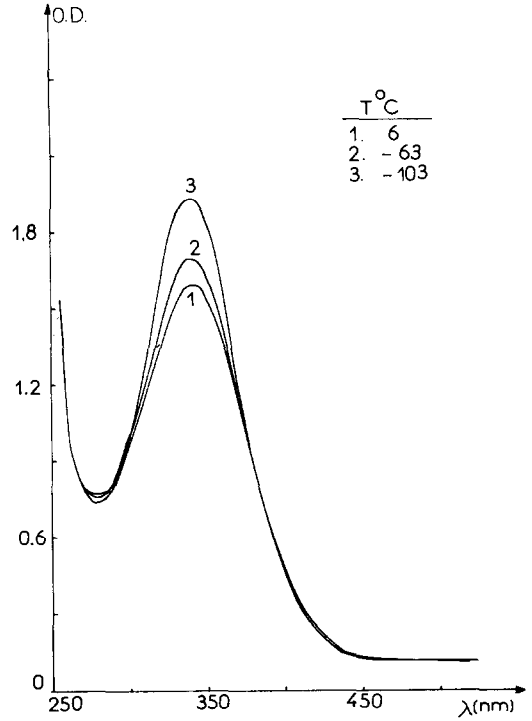


Fig. 2. Effect of temperature on the spectral absorption of dicumylbarium in THF.

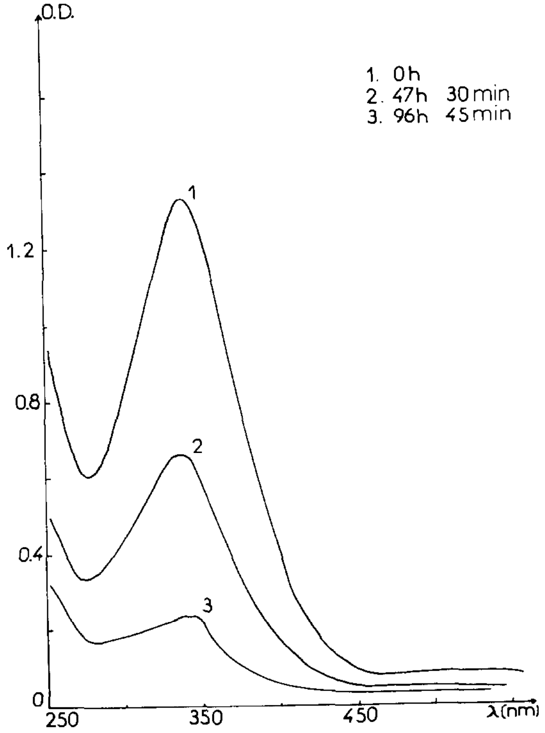


Fig. 3. Stability of dicumylbarium in THF at 22°C.

Conductance studies

Figure 4 depicts the temperature dependence of the equivalent conductance (Λ) of dicumylbarium at different concentrations (c) in THF. For a given concentration, the equivalent conductance increases linearly with temperature. At a constant temperature it increases with decreasing concentration. However, dissociation of the salt is weak and it is impossible to evaluate the values of limiting equivalent conductance (Λ_0) directly from the Kraus-and-Bray's equation $1/\Lambda = 1/\Lambda_0 + c\Lambda/K_1\Lambda_0^2$ in which K_1 is the dissociation constant of ion pairs. These values are prerequisites to application of the Fuoss's equation [19]:

$$F/\Lambda = 1/\Lambda_0 + f^2 c\Lambda/FK_1\Lambda_0^2.$$

Based on the published value for the polystyryl anion [20], we estimated the $\Lambda_0 = \lambda^+_{0(\mathrm{Cm}^-\mathrm{Ba}^{2+})} + \lambda^-_{0(\mathrm{Cm}^-)}$ of dicumylbarium at 15°C to be 70 Ω^{-1} cm^2 mol^{-1}. At other temperatures, the Λ_0's were deduced from Walden's rule: $\eta\ \Lambda_0 = $ constant, where η represents the viscosity of the solvent. The viscosity and dielectric constant of THF at any particular temperature from 15 to −70°C were taken from the literature [1]. The resulting Fuoss plots are shown in Fig. 5 and give a series of curves whose intercepts are indistinguishable from zero. As in the case of polystyryl

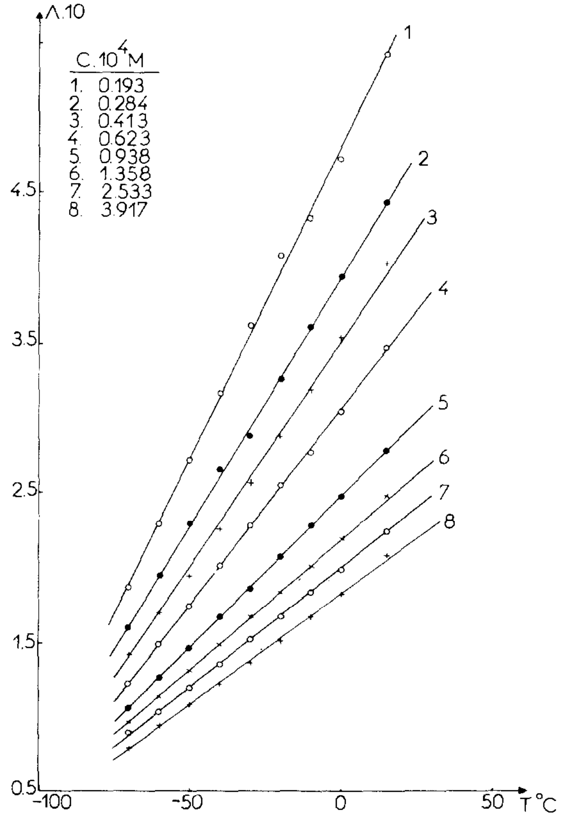


Fig. 4. Variation of the equivalent conductance of dicumylbarium with temperature at different concentrations in THF.

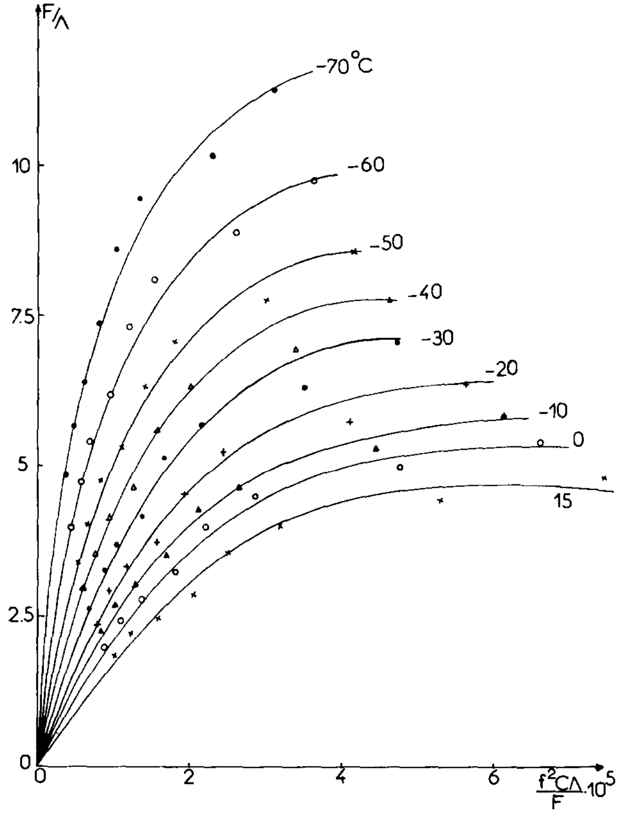


Fig. 5. Fuoss plots for dicumylbarium in THF.

barium [12], such deviation from linearity is attributed to the formation of triple ions; i.e.

$$(\mathrm{Cm}^-)_2\mathrm{Ba}^{2+} \overset{K_1}{\rightleftharpoons} \mathrm{Cm}^-\mathrm{Ba}^{2+} + \mathrm{Cm}^- \qquad (1)$$

$$2\,(\mathrm{Cm}^-)_2\mathrm{Ba}^{2+} \overset{K_2}{\rightleftharpoons} \mathrm{Cm}^-\mathrm{Ba}^{2+} + (\mathrm{Cm}^-)_3\mathrm{Ba}^{2+} \qquad (2)$$

$$(\mathrm{Cm}^-)_3\mathrm{Ba}^{2+} \overset{K_T}{\rightleftharpoons} \mathrm{Cm}^- + (\mathrm{Cm}^-)_2\mathrm{Ba}^{2+} \qquad (3)$$

Figure 6 shows plots of $c\Lambda^2$ against c in accordance with the Wooster's equation [21]:

$$c\Lambda^2 = K_1\Lambda_0^2 + \left(2\Lambda_0\lambda_0 - \Lambda_0^2\right)K_2 c$$

These are all straight lines with well-defined intercepts. Hence, the values of K_1 and K_2 at various temperatures can be evaluated. The pertinent data are compiled in Table 1. Also included are the values of Λ_0 and λ_0 used in the calculation. At 15°C, $\lambda_0 = \lambda^+_{0(\mathrm{Cm}^-\mathrm{Ba}^{2+})} + \lambda^-_{0((\mathrm{Cm}^-)_3\mathrm{Ba}^{2+})}$ was estimated to be 59.3.

The dissociation constant for dicumylbarium in THF varies only slightly with

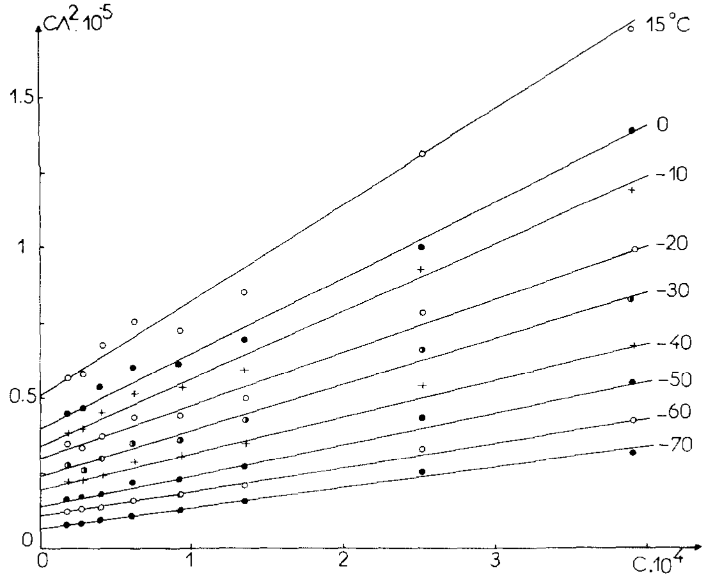


Fig. 6. Wooster plots for dicumylbarium in THF.

temperature. Over the range 15 to −70°C it varies only from 1×10^{-9} to 2.3×10^{-9} *M*. The enthalpy and entropy of reaction obtained from the Van't Hoff plots shown in Fig. 7 are as follows: ΔH_1 −1.1 kcal mol^{-1}, ΔS_1 −45 e.u. for the dissociation of ion pairs and ΔH_2 −1.4 kcal mol^{-1}, ΔS_2 −28 e.u. for the formation of triple ions. The linear dependence of ln K_1 upon $1/T$ is noteworthy. It proves that the existing contact ion pairs are not solvated at low temperature, otherwise there would have been a decrease of enthalpy [22]. The relatively weak exothermicity of the dissociation process compared to the case of alkali cations indicates that the energy required

TABLE 1

DISSOCIATION OF DICUMYLBARIUM

T (°C)	in THF				in THP		
	Λ_0	λ_0	$K_1 \times 10^9$ *M*	$K_2 \times 10^5$ *M*	Λ_0	λ_0	$K_2 \times 10^6$ *M*
15	70.0	59.3	1.04 (1.35) [a]	0.93 (1.26) [a]	40.0	33.9	0.97
10					37.0	31.2	1.05
0	59.2	50.2	1.14	1.03	31.0	26.2	1.09
−10	52.1	44.2	1.28	1.15	25.2	21.2	1.15
−20	45.5	38.6	1.35	1.22	21.0	17.7	1.16
−30	39.3	33.3	1.47	1.40	16.8	14.1	1.21
−40	33.5	28.4	1.60	1.55			
−50	28.1	23.8	1.85	1.82			
−60	23.2	19.7	1.95	2.19			
−70	18.8	15.9	2.26	2.73			

[a] The results in brackets were obtained with a different batch of dicumylbarium prepared separately.

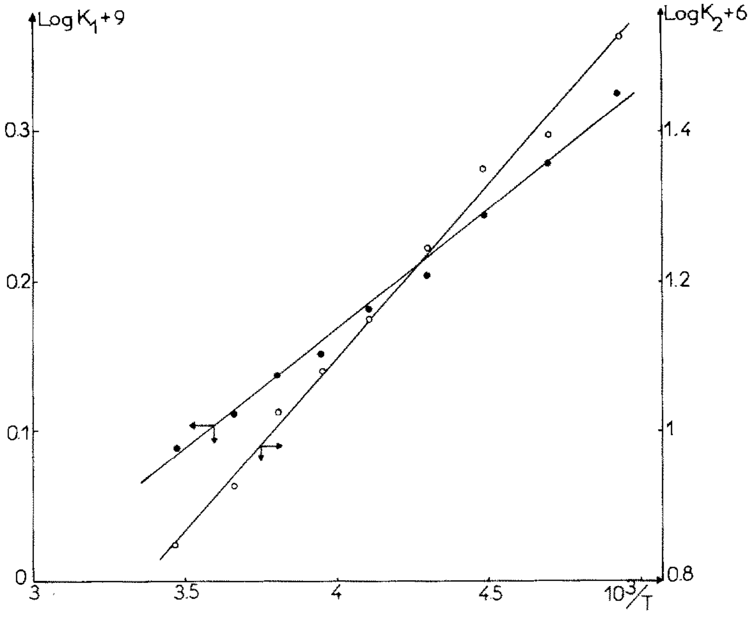


Fig. 7. Van't Hoff plots for dicumylbarium in THF.

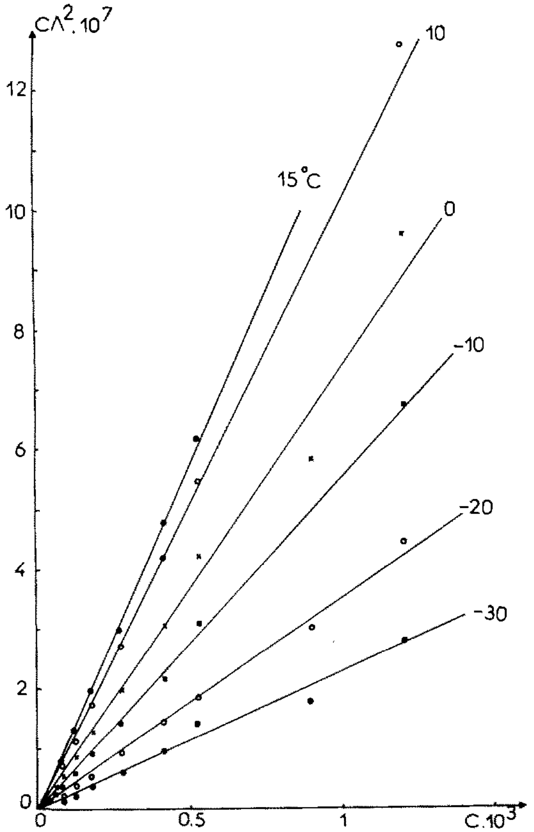


Fig. 8. Wooster plots for dicumylbarium in THP.

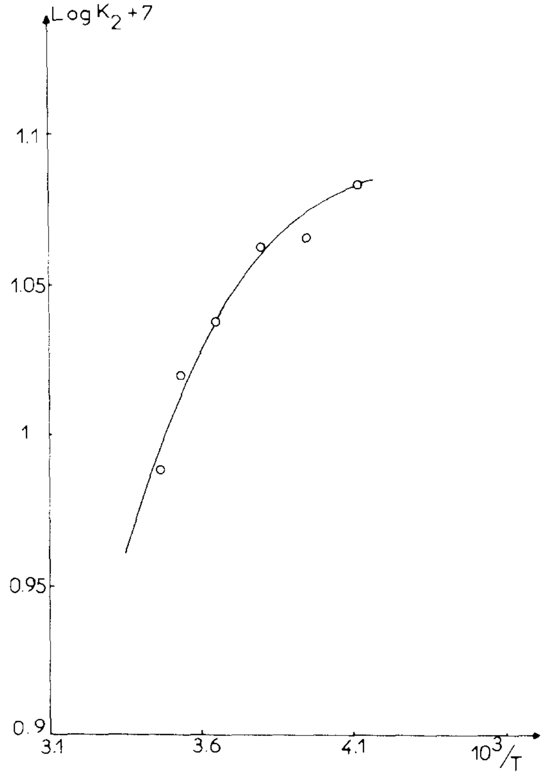


Fig. 9. Van't Hoff plots for dicumylbarium in THP.

to overcome coulombic interaction considerably outweighs any additional gain of energy arising from the solvation of the cation. Similar results were also reported for the dissociation of polystyryl barium [12] and polystyryl strontium [23].

In THP, a solvent of higher viscosity but lower dielectric constant than THF, dissociation of the cumyl salt is too weak to be determined experimentally. As shown in Fig. 8, the Wooster plots are again straight lines but pass through the origin. To compute K_2's from these slopes, Λ_0's were estimated by applying Walden's rule to the corresponding values in THF. The results are presented in Table 1. A plot of $\ln K_2$ versus $1/T$ gives ΔH_2 -1.6 kcal mol^{-1} and ΔS_2 -33 e.u. at 15°C (Fig. 9).

Kinetic studies of proton-transfer reaction

Dicumylbarium reacts with triphenylmethane to form bis(triphenylmethyl)barium and cumene; i.e.,

$$\mathrm{Cm}^- + \mathrm{TmH} \xrightarrow{k_p} \mathrm{Tm}^- + \mathrm{CmH}$$

The rate of reaction is given by:

$$\frac{d}{dt}[\mathrm{Tm}^-] = -\frac{d}{dt}[\mathrm{Cm}^-] = k_p \times [\mathrm{Cm}^-] \times [\mathrm{TmH}]$$

This, after rearrangement and integration, leads to the expression:

$$\ln\frac{[\mathrm{Cm}^-]_0}{[\mathrm{Cm}^-]_t} = k_\mathrm{p} \times [\mathrm{TmH}] \times t$$

in which $[\mathrm{Cm}^-]_0$ and $[\mathrm{Cm}^-]_t$ represent respectively the concentrations of the cumyl salt before and at any instant t of the reaction, [TmH] the concentration of triphenylmethane and k_p the constant of protonation. This can be written as:

$$\ln\frac{\mathrm{OD}_\infty}{\mathrm{OD}_\infty - \mathrm{OD}_t} = k_\mathrm{p} \times [\mathrm{TmH}] \times t$$

where OD_∞ and OD_t denote the optical densities of the triphenylmethyl salt at the end and at any instant t of the reaction. Accordingly, a plot of $\ln(\mathrm{OD}_\infty/\mathrm{OD}_\infty - \mathrm{OD}_t)$ versus t should be a straight line passing through the origin with a slope equal to k_p [TmH], from which k_p can be calculated.

A typical example of the experimental plots is shown in Fig. 10. The reaction is rapid in the beginning but slow towards the end due to the formation of mixed ions. Because of this complication, in our kinetic studies we used only the initial slopes of the plots. The pertinent data are listed in Table 2 and it can be seen that the constant of protonation increases with decreasing carbanion concentration. A plot of the apparent rate versus carbanion concentration is a horizontal straight line with an intercept of 1.65×10^{-5} sec^{-1} (Fig. 11).

As discussed in the previous paragraph, conductimetric measurements revealed that dicumylbarium forms triple ions and that the three thermodynamic equilibrium constants may be related by $K_1 = K_2 \times K_T$. Let c be the concentration of carbanion per liter, $c_\pm$ the concentration of $(\mathrm{Cm}^-)_2\mathrm{Ba}^{2+}$, c_+ the concentration of $\mathrm{Cm}^-\mathrm{Ba}^{2+}$, c_- the concentration of Cm^- and c_T the concentration of $(\mathrm{Cm}^-)_3\mathrm{Ba}^{2+}$. Then,

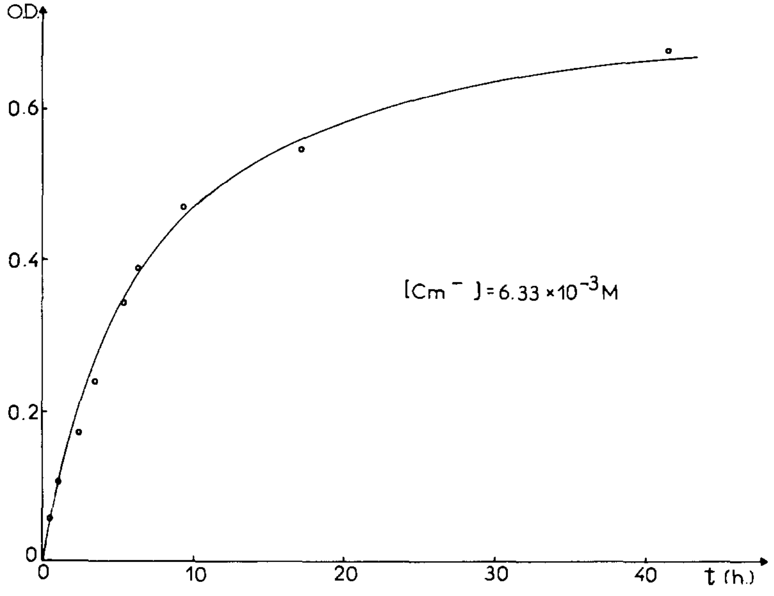


Fig. 10. Rate of conversion of dicumylbarium in the course of protonation.

TABLE 2

PROTONATION OF DICUMYLBARIUM BY TRIPHENYLMETHANE IN THF

Equilibrium no.	$[\mathrm{Cm}^{-1}] \times 10^3$ M	$[\mathrm{TmH}] \times 10^2$ M	$k_p \times 10^3$ M^{-1} sec^{-1}
1	11.0	1.09	1.20
2	10.01	0.80	2.11
3	6.33	1.45	2.02
4	4.84	1.96	3.46
5	3.37	1.05	5.78
6	1.94	1.71	8.12
7	0.95	4.33	17.1
8	0.54	0.24	28.6
9	0.44	0.32	40.9

$c_\pm \simeq c/2$ and $c_+ = c_- + c_T$. From equilibria 1 to 3 (Table 2), the apparent rate of protonation is given by:

$$k_p c = k_{p-} c_- + 2k_{p\pm} c_\pm + 3k_{pT} c_T + k_{p+} c_+$$

This can be shown to lead to the expression:

$$k_p = k_{p-} (K_1 \times K_T)^{1/2} c^{-1} + k_{p\pm} + \tfrac{3}{2}(k_{pT} + k_{p+})(K_1/K_T)^{1/2}$$

where k_p is the rate constant, k_{p-}, k_{p+}, $k_{p\pm}$ and k_{pT} represent respectively the constants of reaction by the corresponding ionic species. For the apparent rate of reaction to be independent of carbanion concentration, the following condition must hold:

$$k_p c = k_{p-}(K_1/K_2^{1/2})$$

i.e. the protonation proceeds exclusively via free ions. By introducing the relevant values of K_1 and K_2 into this equation, the constant of reaction by free ions was found to be k_{p-} 48.4 M^{-1} sec^{-1}. This values is lower than that obtained for the protonation of polystyrene associated with alkali cations, e.g. for $\mathrm{pS^-Na^+}$, k_{p-} 178 M^{-1} sec^{-1} at 25°C [24]. It may be explained by increased steric hindrance due to the presence of a methyl group in the cumyl anion.

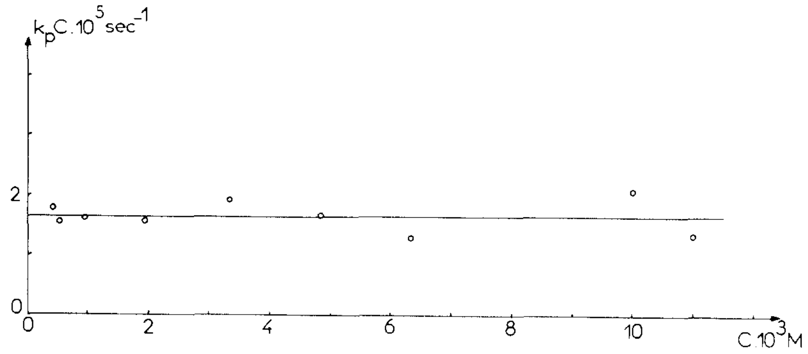


Fig. 11. Variation of apparent rate of protonation with carbanion concentration.

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