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METAL-STABILIZED CARBANIONS

II *. KINETIC ACIDITY AND NMR SPECTRA OF THE π-(TRICARBONYLCHROMIUM)-FLUORENYL ANION

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Summary

The rate of deprotonation of fluorene and of π-(tricarbonylchromium)-fluorene by an excess of KH in THF was measured by monitoring the hydrogen evolution. The pseudo-first order rate constant for the complex is ca. one order of magnitude higher than that for the free ligand. ^{1}H and ^{13}C NMR analysis showed that when the anion is produced at —20°C or below, the $Cr(CO)_3$ group is bonded to one of the phenyl rings (η^6-anion), whereas ionization at room temperature produces solutions containing mainly the anion with the $Cr(CO)_3$ bonded to the cyclopentadienyl ring (η^5-anion) in equilibrium with the η^6-isomer. The effect of ionization on free and complexed systems, together with the effect of complexation of the free anion, is discussed on the basis of the NMR data. The $\eta^6 \rightleftharpoons \eta^5$ isomerization equilibrium was followed at various temperatures and different degrees of solvation are deduced for the two isomeric ion pairs from the kinetic and thermodynamic solvation parameters.

Introduction

Coordination of a tricarbonylchromium (TCC) unit to an aromatic ring via π-bonding increases the acidity of groups bonded to the α carbon of the side chain. Thus, the pK_a of complexed benzoic acids [2], phenols [3] and

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* For part I, see Ref. 1. Portions of this work have been reported at the 12th Congresso Nazionale di Chimica Organica, September 1980, Ancona (Italy). Abstract p. 257.

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anilinium salts [4] are much lower than those of the corresponding free ligands.

The presence of the TCC group increases the rate of the β-elimination from 2-phenylethyl compounds catalyzed by bases, by an amount which depends on the nature of the leaving group and the solvent-base system [5]. The important feature is that transition states with a high degree of carbanionic character at the α carbon are greatly stabilized by the coordination of the aromatic ring with chromium.

It follows that carbanions α to a TCC-complexed aromatic ring should be produced without difficulty and should be easy to study by direct spectroscopic observation. Despite this, until now there have been only a few examples of the formation and NMR spectroscopic investigation of TCC-arylalkyl carbanions. Two systems, to our knowledge, have been examined: the TCC-fluorene and its anion in dimethylsulfoxide in a PMR study [6] and the bis(TCC)$_2$-diphenylmethyl carbanion in ^{13}C NMR investigation [7]. The TCC-indenyl and -fluoreny anions, their syntheses and reactions have been recently investigated by Nesmeyanov et al. [8a,b], and recent publications [8c,d] have dealt with the isomerization of the η^6- to η^5-TCC-fluorenyl carbanion, which was monitored by IR spectroscopy. In addition, the ^{1}H NMR spectra of the two fluorenyl carbanion isomers in THF-d_8 have been described [28]. This publication prompted us to communicate our results obtained by ^{13}C and ^{1}H NMR spectroscopy for the same fluorenyl system under different conditions. The results on TCC-complexe carbanions of benzylic structure will be described in a later paper.

Results

(a) Production of the anions

Of the various methods employed to prepare solutions of the uncomplexed arylalkyl carbanions for charge distribution studies by spectroscopic techniques the reaction of the hydrocarbons with n-butyllithium in ethereal solvents is the most used [9]. Unfortunately, this method is not appropriate for the complexed substrates since an aryl ring coordinated with TCC is so activated toward carbon bases that abstraction of an exocyclic hydrogen may become less important than the ring alkylation [1]. Metalation of fluorene and its complexed derivative was thus carried out by reaction of the hydrocarbons with potassium hydride in THF, the method used by Buncel [10] for metalation of weak carbo acids in the presence of 18-crown-6 ether, which increases the reactivity of H$^-$ toward the hydrocarbon *. The fluorenyl anions, both complexed and free, were formed rapidly in quantitative yield in the absence of 18-crown-6 ether, and the rates were monitored by measuring the evolution of hydrogen gas. The solvent-base system is not completely inert at room temperature [11], and gas is evolved even in the absence of fluorene substrates; but the rate is so low (ca. 0.2 ml/h at 303 K) that no correction to the fluorene data was needed.

First-order kinetics are well obeyed up to at least 80% of reaction under the conditions specified in the Experimental section. The calculated pseudo first-

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* Metalation of the complexed ring can be excluded in the case of fluorenyl substrate. However, possible competition of the complexed ring hydrogens and the exocyclic hydrogens for H$^-$ cannot be neglected a priori with arylalkyl hydrocarbons less acidic than fluorene.

order rate constants, $k(H_2)$, are: 1.14 × 10^{-2} and 11 × 10^{-2} s^{-1} at 303 ± 0.2 K for free and complexed compounds, respectively.

(b) NMR measurements

The ^1H and ^{13}C data for free and complexed fluorene together with those of the uncomplexed fluorenyl potassium in THF-d_8 are listed in Table 1 and 2. They are in accord with published data [6,12—14].

As far as the ionization products of the TCC-fluorene are concerned, the spectra are strongly dependent upon the temperature. Thus, when the anion is produced at —20°C or below, the ^1H NMR spectrum (Fig. 1a) consists of one singlet at δ 5.58 ppm and two AMPX systems (integral ratio 1/4/4). The chemical shifts and the coupling constants, obtained by a first-order analysis and refined by a modified version of the LAOCOON III program [15], are listed in Table 1. Quenching of the red solution with cold, oxygen-free aqueous THF-d_8 regenerates the original yellow solution of TCC-fluorene which was identified

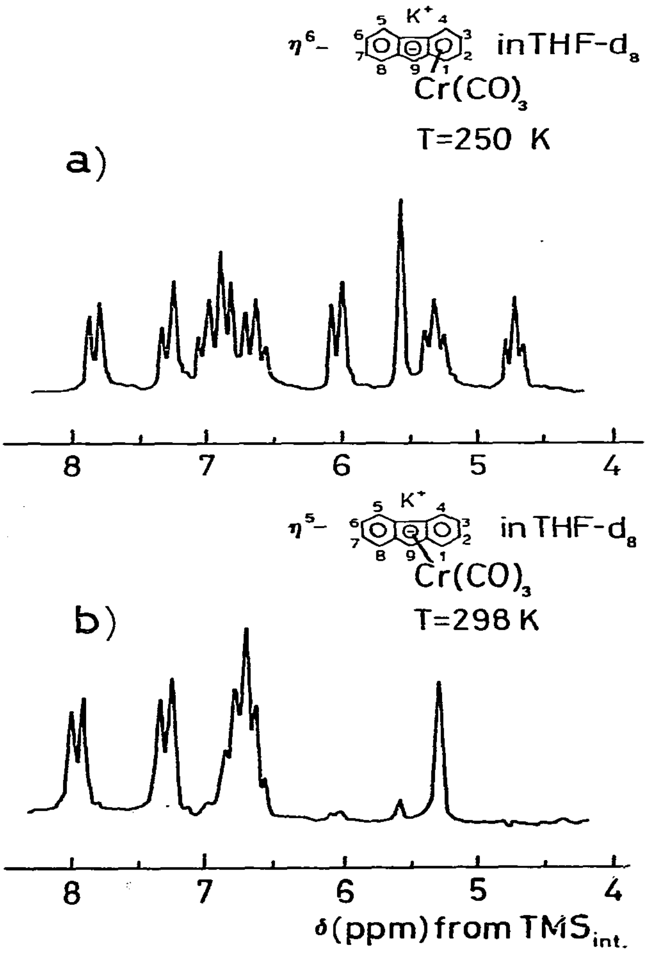
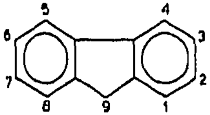
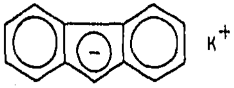
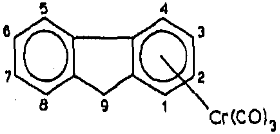
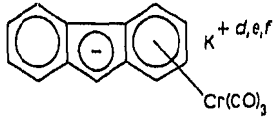
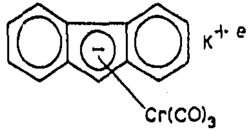


Fig. 1. ^1H NMR spectra of the TCC-flourenyl anion in THF-d_8 obtained (a) at —23°C: (b) at 25°C.

TABLE 1

^{1}H NMR CHEMICAL SHIFTS [a] AND COUPLING CONSTANTS [b] OF FREE AND $Cr(CO)_3$-COMPLEXED FLUORENE AND POTASSIUM FLUORENIDE IN THF-d_8 [c]

	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	δ_9	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{25}
	7.51	7.27	7.34	7.76	7.76	7.34	7.27	7.51	3.87						
	7.27	6.81	6.44	7.86	7.86	6.44	6.81	7.27	5.89	8.09	0.95	0.68	6.64	1.17	7.80
	6.0	5.3	4.7	6.5	7.9	←	7.6	→	4.01						
	6.04	5.31	4.74	6.84	7.82	6.65	6.99	7.33	5.58	6.6	<1	<1	6.0	<1	6.5
	7.30	6.79	6.65	8.00	8.00	6.65	6.79	7.30	5.29	7.6	<1	<1	6.2	<1	8.4

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[a] In ppm from internal TMS. [b] In Hertz. [c] At room temperature, unless otherwise indicated. [d] At −20°C. [e] Line-width is ca. 3 Hz. [f] J_{56} 7.7 Hz; J_{67} 7.0 Hz; J_{78} 7.3 Hz; J_{57}, J_{58}, J_{67}, J_{68} and J_{78} are <1 Hz.

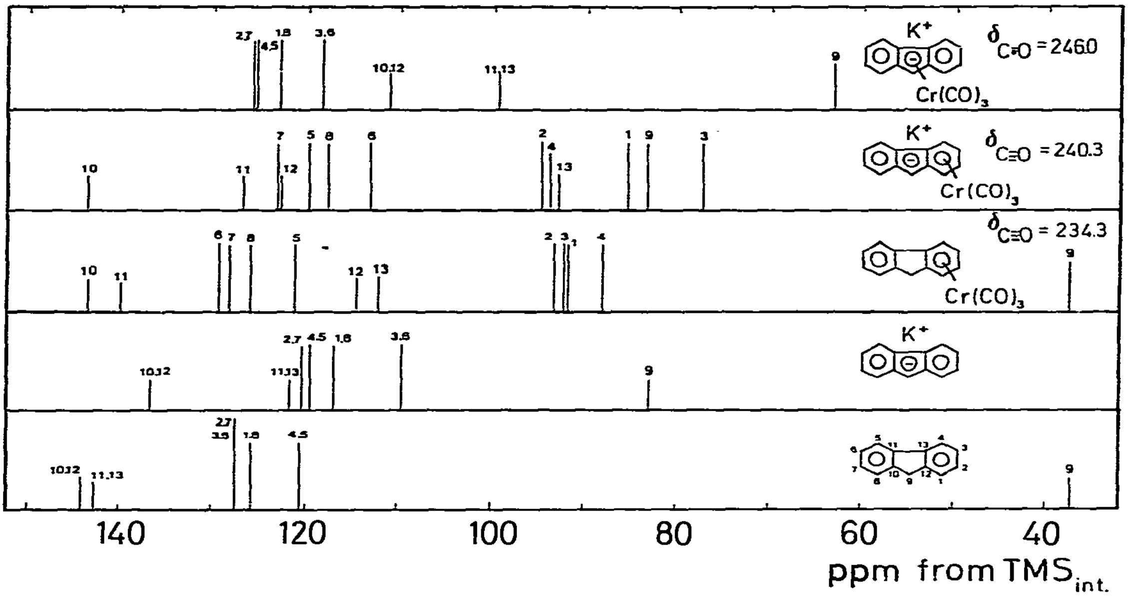

Fig. 2. Schematic ^{13}C NMR spectra of the free and complexed fluorenes and of the corresponding anions.

by NMR spectroscopy and TLC analysis. In contrast, when the anion is produced at room temperature, the ^{1}H NMR spectrum (Fig. 1b) exhibits one singlet at δ 5.29 ppm and an ABMX system (integral ratio 1/8). The spectral parameters are obtained as above and are shown in Table 1, quenching of this solution with aqueous THF regenerates in the original complexed fluorene even in this case. Our ^{1}H NMR data are in good agreement with those previously reported [8d].

If the solution produced at low temperature is warmed to 0°C or above, the spectrum changes with the time into that obtained by ionization at room temperature.

Very similar results were obtained by ^{13}C NMR spectroscopy: ionization of TCC-fluorene at —20°C gives a fourteen-line spectrum which, on warming, changes into an eight-line spectrum identical to that obtained by ionization at room temperature. The ^{13}C chemical shifts and the ^1J(C—H) coupling constants are listed in Table 2. Figure 2 shows the ^{13}C spectra of the hydrocarbons and the respective anions as a stick diagram.

(c) Kinetics of the isomerization

The isomerization was followed by ^{1}H NMR measurements (in the pulsed FT-mode *) at three temperatures. The relative amounts of the two anionic species and the final concentration ratios were calculated by comparison of the integrals of the signals relative to the two isomeric species. The very high signal-to-noise ratio led to good accuracy in the integral determinations.

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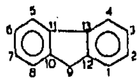
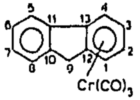
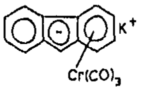
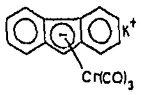
* To enable accurate comparisons of the areas, the spectra were recorded under fully relaxed conditions.

TABLE 2

^{13}C NMR CHEMICAL SHIFTS [a] (AND ^1J(C—H) COUPLING CONSTANTS [b]) FOR FREE AND Cr(CO)$_3$-COMPLEXED FLUORENE AND POTASSIUM FLUORENIDE IN THF-d_8 [c]

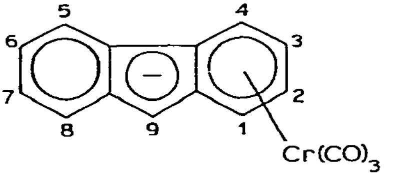
			Δδ [d]			Δδ [d, e]		Δδ' [f]
C(1)	125.5 (162)	116.8 (154)	−8.7	91.6 (175)	85.2 (164)	−6.4	122.6 (156)	+5.8
C(2)	127.3 (159)	120.2 (154)	−7.1	93.1 (175)	94.5 (164)	+1.4	125.4 (159)	+5.2
C(3)	127.3 (159)	109.5 (156)	−17.8	92.0 (175)	77.1 (171)	−14.9	118.1 (157)	+8.6
C(4)	120.4 (159)	119.4 (150)	−1.0	97.9 (176)	93.5 (167)	+5.6	125.2 (159)	+5.8
C(5)	120.4 (159)	119.4 (150)	−1.0	120.9 (157)	119.5 (153)	−1.4	125.2 (159)	+5.8
C(6)	127.3 (159)	109.5 (156)	−17.8	129.1 (158)	113.0 (165)	−16.1	118.1 (157)	+8.6
C(7)	127.3 (159)	120.2 (154)	−7.1	127.9 (160)	122.7 (154)	−5.2	125.4 (159)	+5.2
C(8)	125.5 (162)	116.8 (154)	−8.7	127.5 (160)	117.6 (154)	−8.1	122.6 (156)	+5.2
C(9)	37.3 (129)	82.9 (160)	+45.6	37.5 (132)	83.1 (166)	+45.6	63.0 (176)	−19.9
C(10)	144.0 (—)	136.5 (—)	−7.5	143.2 (—)	143.3 (—)	+0.1	110.9 (—)	−25.6
C(11)	142.0 (—)	121.5 (—)	−21.0	139.7 (—)	126.6 (—)	−13.1	99.1 (—)	−22.4
C(12)	144.0 (—)	136.5 (—)	−7.5	114.3 (—)	122.6 (—)	+8.3	110.9 (—)	−25.6
C(13)	142.0 (—)	121.5 (—)	−21.0	112.0 (—)	92.7 (—)	−19.3	99.1 (—)	−22.4
C≡O	—	—	—	234.3 (—)	240.3 (—)	+6.0	246.0 (—)	—

[a] In ppm from internal TMS. [b] In Hertz (given in parentheses). [c] At room temperature unless otherwise indicated. [d] $\Delta\delta = \delta_{\text{ion}} - \delta_{\text{neutral}}$. [e] At −20°C. [f] $\Delta\delta' = \delta_{\eta\text{anion}} - \delta_{\text{free anion}}$.

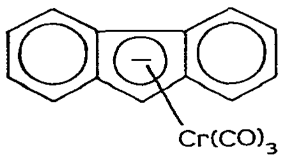
Use of the equation for a first-order irreversible reaction gave satisfactory plots up to 50—60% reaction, but at higher percentage of reaction a definite decrease of the rate constant was evident. This was not observed when the kinetic data were analysed in terms of a first-order equilibrium rate equation, very good linearity being observed up to at least 80% reaction. The rate constants, k, and the activation parameters for the direct and reverse process, together with the equilibrium constants, K_{eq}, are shown in Table 3.

Discussion

The ^1H and ^{13}C NMR spectra of the TCC-fluorenyl anion obtained at —20°C clearly indicate that TCC is bonded to one of the phenyl rings (η^6-isomer, I).



(I)



(II)

Selective deuteration of the 9-position allowed the unambiguous assignment of the H(9) and C(9)-resonances.

Moreover, the ^1H and ^{13}C spectra consist of two sets of signals. The set of lower field exhibits chemical shifts and coupling constants very similar to those shown by the free potassium fluorenide and it thus attributed to the atoms of the uncomplexed phenyl ring; the higher field set of peaks is then attributed to the atoms of the complexed phenyl ring. The peak assignment of the various positions was carried out for the ^1H nuclei by means of double resonance experiments and for the ^{13}C atoms by means of undecoupled and partially relaxed spectra.

The spectra obtained at room temperature are attributed to the symmetrical η^5-TCC-fluorenyl anion (II) because of the presence of two equivalent phenyl rings, for which a set of J(H—H) and ^1J(C—H) coupling constants typical for an uncomplexed phenyl ring [16] are observed, and because of the upfield shift of the five-membered ring carbons typically induced by the TCC entity [17]. In addition, the $^{13}C{\equiv}O$ resonance is shifted downfield relative to that of the η^6-isomer.

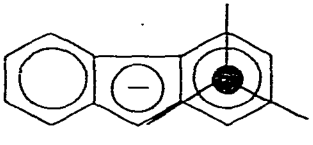
The ^{13}C NMR data allow study of the effect of the complexation on neutral and charged systems and also of the effect of the ionization on the free and complexed fluorene. The complexation of the neutral fluorene exhibits the well known upfield shifts (ca. 34 ppm) of the protonated carbons of the complexed ring together with an increase of the ^1J(C—H) coupling constants [16]; on the other hand, the uncomplexed moiety shows small shifts as observed for other hydrocarbons [17].

In the case of the η^6-anion, the ionization effect ($\Delta\delta = \delta_{ion} - \delta_{neutral}$, see Table 2) on the chemical shifts of all the protonated carbon atoms (except C(2) and C(4)) is very similar for free and complexed systems. In particular, the $\Delta\delta$ values are identical for the C(9) atom. This seems to indicate that coordination of the phenyl ring has little effect on the charge distribution on the whole organic skeleton and, in particular, on the C(9) carbon, where, in the uncomplexed ion, the negative charge density is mainly localized [18].

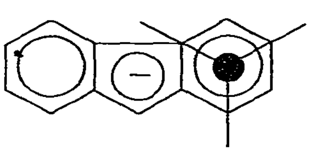
This consideration is in accord with the effect of the TCC complexation on the kinetic acidity of the fluorene as measured by the H_2 evolution rate, $k(H_2)$. The experimental ratio, $k(H_2)_{complex}/k(H_2)_{free} = 9.6$, is not high and confirms that, as shown for the diphenylmethyl cations [19], the magnitude of the TCC effect on the stability of charge intermediates is strongly dependent upon their intrinsic stability: i.e., the fluorenyl anion is a rather stable species by itself and so the coordination has a relatively small effect on the acidity. Much larger effects have been observed for the rate of formation of carbanions of benzylic structure much less stable than the fluorenyl anion [20],

The C(2) and C(4) atoms of the complexed ring, which may be regarded as "*meta*" to the 9-position, show positive $\Delta\delta$ values (+1.4 and +5.6 ppm, respectively), whereas the corresponding $\Delta\delta$ values for the uncomplexed system are negative (—7.1 and —1.0 ppm, respectively). This significant deshielding of the *meta*-positions is in line with that found for a series of TCC-arenes bearing strong electron-releasing substituents, and has been attributed to the transmission of mesomeric effects not only to the *ortho*- and *para*-, but also to the *meta*-positions [21]. Thus, the C(9) atom behaves as a powerful electron-releasing group. The downfield shift of the carbonyl resonance support this conclusion, and agree with literature data [22] concerning the effect of substituents on $^{13}C{\equiv}O$ chemical shifts. The experimental value ($\Delta\delta(^{13}C{\equiv}O) = +6.0$ ppm) is equal in magnitude, but opposite in sign, to the equivalent $\Delta\delta$ value found for the TCC-complexed arylmethyl carbenium ions [23].

Finally, in the light of the reports by Roques et al. [24], the deshielding of C(2), C(4) and C(12) in the η^6-complexed fluorenyl anion with respect to the free system indicates that, under our conditions, of the two conformation, III and IV, that with the carbonyls eclipsed to the negative C(9) (i.e., III) is preferred.



(III)



(IV)

When the TCC is bonded to the five-membered ring of the fluorenyl anion, the comparison of the ^{13}C chemical shifts between the complexed and uncomplexed anions indicates a well-defined downfield shift for all the protonated carbon resonances of the uncomplexed rings and a strong upfield shift of the carbons of the cyclopentadienyl system. In addition, the $^{13}C{\equiv}O$ carbon atoms resonate at nearly the same frequency as those shown by the carbonyls of the TCC-cyclopentadienyl sodium (δ 246.9 ppm) [25].

These results suggest that appreciable charge transfer occurs from the external rings into the cyclopentadienyl ring, and from this into the inorganic moiety.

Kinetic data

As noted in the Introduction, the equilibrium and the kinetics of interconversion of the two isomeric structures of the TCC-fluorenyl anion have been very recently investigated [8c,d] by IR spectroscopy. In THF it was found that the equilibrium constant depends upon the nature of the cation and the presence of cation-solvating additives such as the dicyclohexyl-18-crown-6 ether. It is of interest to compare our results obtained by NMR-measurements on solutions at least thirty times more concentrated with those obtained in the IR studies.

Good agreement is found between our and Nesmeyanov's data concerning the isomerization rate constants, $k(\eta^6 \rightarrow \eta^5)$. On the other hand, our results on the equilibrium constants, K_{eq}, and the $k(\eta^5 \rightarrow \eta^6)$ rate constants are somewhat different. Moreover, the Arrhenius plots of our kinetic constants give straight lines with a very good correlation coefficient ($r \geqslant 0.9998$). The calculated activation parameters (see Table 3) differ from those reported by Nesmeyanov, which were calculated from Arrhenius plots with poorer correlation coefficients ($r \leqslant 0.974$). The differences between ours and Nesmeyanov's results are only in magnitude, not in sign, so that the shift of the equilibrium, as determined by the reaction parameters ΔH and ΔS, can be interpreted similarly: i.e. the TCC-fluorenyl anion isomerization is an entropy-controlled process, which, at the various temperatures and concentrations investigated, favours the η^5-isomer. In fact, the noticeably entropy variation (ΔS = +18.6 e.u.) for the reaction overcomes the effect of the corresponding enthalpy change (ΔH = +4.3 kcal mol^{-1}).

It is well known [27] that when ionic species are dissolved in ether, the medium solvates the cationic much more strongly than the anionic partner of the pair. Thus, the variations of the thermodynamic parameters for this type of solutions are generally attributed to changes of interaction between the acidic cation and the basic solvent.

The unimolecular, internal migration of the TCC in the fluorenyl anion, which is probably a concerted process, is not expected to induce large entropy variations arising from the distribution of the charge and the solvation on the anion. Therefore the much greater negative value for $\Delta S(\eta^5 \rightarrow \eta^6)$ with respect to the $\Delta S(\eta^6 \rightarrow \eta^5)$ can be explained in terms of different degrees of solvation

TABLE 3

RATE CONSTANTS [a] AND ACTIVATION PARAMETERS FOR THE ISOMERIZATION EQUILIBRIUM BETWEEN η^6 AND η^5-TCC-FLUORENYL POTASSIUM

T (K)	$10^5\ k(\eta^6 \rightarrow \eta^5)$ (s^{-1})	$10^5\ k(\eta^5 \rightarrow \eta^6)$ (s^{-1})	K_{eq} [b]
273	5.5	1.4	3.97
283	20.0	4.8	5.25
293	68.0	10.0	6.80
Parameters		$\eta^6 \rightarrow \eta^5$	$\eta^5 \rightarrow \eta^6$
$\Delta H^{\neq}$ (kcal/mol) [c]		19.4	15.1
$\Delta S^{\neq}$ (e.u.) [d]		−6.8	−25.4

[a] Errors in the calculation of the rate constants are ≤4%. [b] ±2%. [c] ±1 kcal mol^{-1}. [d] ±1.5 e.u.

around the K^+ ion in the two isomers. In particular, the entropy values indicate a higher degree of reorganization of the solvent around the K^+ ion starting from the η^5-anion than from the η^6-anion. The conclusion would be that the $[\eta^5]^- K^+$ ion pair is less solvent-separated than the $[\eta^6]^- K^+$ ion pair. This interpretation is supported by the ^{13}C NMR data, which indicate that the negative charge is less dispersed in the η^5- than in the η^6-structure.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH-90 FT-spectrometer equipped with a Bruker B-ST 100/700 temperature control apparatus. TMS was used as internal standard. The TCC complexes of 9,9-fluorene-h_2 (Aldrich) and 9,9-fluorene-d_2 [26] were made in diglyme by standard methods and purified by crystallization from THF/hexane under argon.

Free and TCC-fluorenyl anion solutions for NMR measurements were prepared under dry argon at the appropriate temperature by treating ca. 0.3 M solutions of the hydrocarbons in anhydrous, oxygen-free THF-d_8 with an excess of KH (Fluka, freed from mineral oil by repeated washings with dry cyclohexane). The resulting suspension was allowed to settle and the clear solution was cautiously transferred under argon into the NMR tube maintained at the same temperature.

H_2 gas evolution was monitored by means of a gas burette when ca. 10^{-2} M solutions of the hydrocarbons in THF were treated with an excess of KH (suspended in THF) under argon at 303 K.

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