Theoretical Investigation on the Structure of 9-Anthrylmethyl Cation

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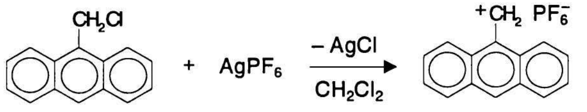
The structure of the cationic polymerization initiator 9-anthrylmethyl cation is studied. By means of quantum-chemical calculations the bands in the UV region characteristic of this cation are assigned. It is shown that the changes in its electronic spectrum are caused by structural changes.

9-Anthrylmethyl hexafluorophosphate prepared by the interaction shown in Scheme 1 is a stable primary carbenium salt which initiates the polymerization of vinyl and heterocyclic monomers with low reactivity such as styrene, isobutene, 1,2-dimethoxyethylene, and 4-methyl-1-pentene [1, 2]. This initiator has higher reactivity than trityl and diphenylmethyl salts. Its spectral characteristics, initiation ability and initiation mechanism of polymerization of α-methylstyrene and *p*-methoxystyrene were studied in previous papers [2, 3]. The high reactivity of the cation may be followed by changes in the electronic spectra of the initiator solutions. The interest in this initiator is also arisen by its photoreactivity. On irradiation with the light at λ = 366 nm it forms dimers [4]. This reaction was used for intra- and intermolecular cyclization of oligomers [5, 6].



Scheme 1

The aim of this work is to study further the structure of 9-anthrylmethyl cation and the reasons for the changes in its electronic spectrum.

EXPERIMENTAL

9-Chloromethylanthracene (Fluka) was recrystallized and dried *in vacuo*. Silver hexafluorophosphate (Fluka) was dried *in vacuo*. Methylene dichloride was distilled and dried over CaH_2 and $LiAlH_4$ on a vacuum line.

The preparation of 9-anthrylmethyl hexafluorophosphate was carried out by mixing of methylene dichloride solutions of 9-chloromethylanthracene and $AgPF_6$ *in vacuo* (6.67×10^{-4} Pa) at room temperature. The reaction mixture became immediately bright orange in colour. The precipitate of AgCl was removed.

Although the MNDO method [7, 8] was parametrized to reproduce ground-state properties of neutral molecules, it also gives good results for positive and negative ions [9]. An exception are the ions where the charge is concentrated on one atom [10].

The full geometry optimizations of all the studied compounds were carried out by means of the MNDO method [7] using Davidon—Fletcher—Powell procedure with MNDOC program package [11]. The CNDO/S-CI method [12, 13] was used to predict the UV spectrum of the anthrylmethyl cation ACH_2^+.

RESULTS AND DISCUSSION

9-Anthrylmethyl cation (ACH_2^+) is formed from 9-chloromethylanthracene (ACH_2Cl) after abstraction of chloride ion Cl^-. The stability of this primary carbenium ion is due to the delocalization of the positive charge on the anthryl fragment. In addition, it forms an ion pair with the stable counter ion, PF_6^- [2]. We assumed that the process

$$ACH_2Cl \rightarrow ACH_2^+ + Cl^-$$

is nonadiabatic, *i.e.* it is so fast that the geometry of the anthrylmethylene skeleton ACH_2 does not change after abstraction of Cl^- from ACH_2Cl. Therefore after the MNDO geometry optimization of ACH_2Cl, a single SCF calculation for ACH_2^+ at the same geometry of anthrylmethylene skeleton was carried out. The energetic effect of the process is calculated to be 573.2 kJ mol^{-1}. The difference in the heats of formation for ACH_2^+ cation after the abstraction of Cl^- from ACH_2Cl and ACH_2^+ in equilibrium state (ACH_2^+(eq)) which is 139.3 kJ mol^{-1} represents the energy of reorganization (in vapour phase) for ACH_2^+ at the transition from nonadiabatic to equilibrium state.

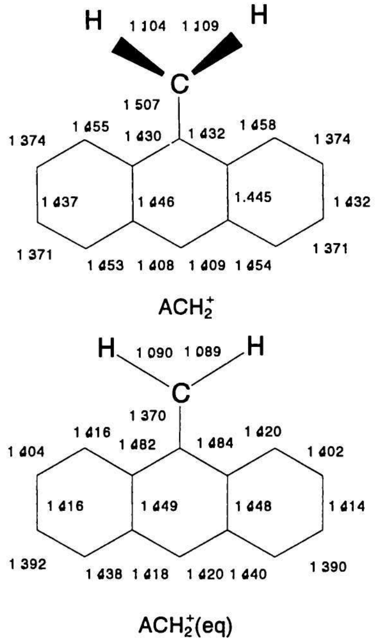
Table 1. Heats of Formation (kJ mol^{-1}) and Charge of the Aliphatic Carbon Atom of the Compounds Studied

Compound	H_f(MNDO) kJ mol^{-1}	$q(CH_2)/e$
ACH_2Cl	209.2	0.183
ACH_2^+	1151.0	0.209
ACH_2^+(eq)^a	1011.7	0.140
Cl^{-b}	− 229.8	

a) H_f(AM1) = 1025.1 kJ mol^{-1} [14]; *b)* H_f(exp.) = − 233.9 kJ mol^{-1} [10].

The control experiments proved that even the "aged" initiator ACH_2^+(eq) preserves its initiation ability. The higher reactivity of the cation obtained *in situ* correlates with the more positive net charge of the aliphatic carbon atom of ACH_2^+ in comparison with ACH_2^+(eq) (Table 1).

The structural changes occurring as a result of the abstraction of Cl^- from ACH_2Cl and the formation of the cation ACH_2^+ are mainly expressed in an intensive shortening of the exocyclic carbon bond by 0.137 Å and prolongation of its neighbouring carbon bonds (see formulas). The methylene group is situated in the plane of the anthryl fragment. Slight deviations from the planar geometry were found for the anthrylmethyl cation. This result is in agreement with the AM1 calculations by *Ford* and *Hermann* [14]. According to these authors, this is a nonplanar structure with a vertical symmetry plane.



ACH_2^+

ACH_2^+(eq)

MNDO calculated structures of the anthrylmethyl cation.

The electronic spectrum of 9-anthrylmethyl hexafluorophosphate in methylene dichloride at room temperature is shown in Fig. 1. Calculations with CNDO/S method were carried out for interpretation of the electronic spectrum of ACH_2^+. These calculations show that the bands at λ = 476.8 nm and 373 nm might be caused by electron transitions in nonadiabatic structure of ACH_2^+ cation, while the bands at λ = 401.1, 392.9, and 354 nm are probably associated with electron transitions in ACH_2^+(eq) (Fig. 1).

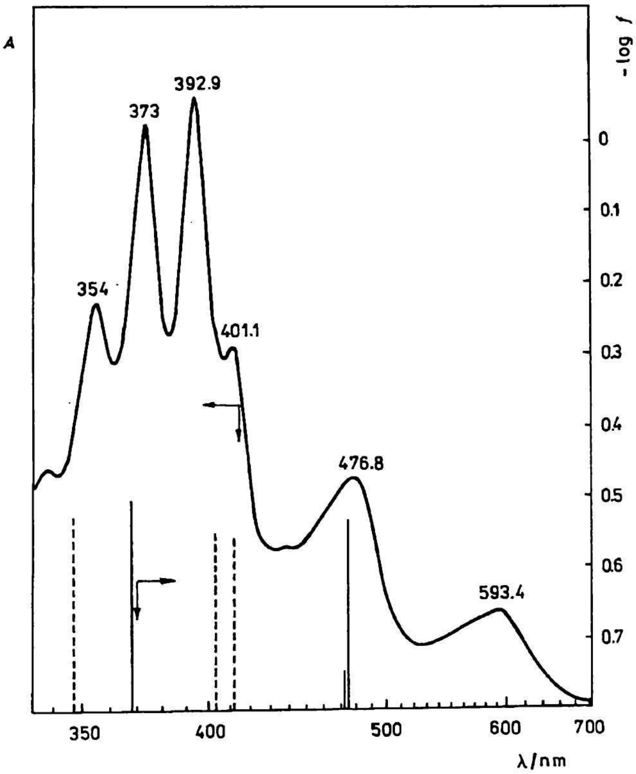


Fig. 1. Electronic spectrum of 9-anthrylmethyl hexafluorophosphate in methylene dichloride at room temperature. The CNDO/S-CI computed transitions are marked by lines: solid line – ACH_2^+, dashed line – ACH_2^+(eq).

The bands at λ = 392.9, 373, and 354 nm are characteristic of all compounds containing anthrylmethyl (ACH_2—) group (*e.g.* the spectra of ACH_3 and ACH_2Cl). Probably the initiator exists in two forms, ACH_2^+ and ACH_2^+(eq), and its spectrum is superposition of the bands of these two cation forms. The band at λ = 593.4 nm is not interpreted because it is not characteristic of anthracene derivatives and of the cationic forms as it remains unchanged after the reaction vessel is opened and the cation is desactivated [2]. Probably this band is due to side condensation products or complexes [3].

The influence of the configuration interaction (CI) on the calculated energy of the electron transitions (λ), the values of the oscillator strengths f, and the percentual share (> 7 %) of the monoexcited configurations V_i^j (i — occupied MO, j — unoccupied MO) in the CI calculated spectral bands are shown in Table 2. For CI = 240, 16 occupied MO's and 15 unoccupied MO's were included in CI. For CI = 525

Table 2. Influence of the Configuration Interaction (CI) on the CNDO/*S*-CI Calculated Electron Transitions of ACH_2^+

Compound	CI = 240			CI = 525			CI = 980		
	λ/nm	*f*	V/l%	λ/nm	*f*	V/l%	λ/nm	*f*	V/l%
ACH_2^+	459.8	0.105	84 ($V_2^{1'}$), 8 ($V_3^{1'}$)	463.7	0.105	84 ($V_2^{1'}$), 8 ($V_3^{1'}$)	472.9	0.292	64 ($V_1^{1'}$), 23 ($V_2^{1'}$)
	440.4	0.363	90 ($V_1^{1'}$)	447.5	0.364	90 ($V_1^{1'}$)	472.0	0.180	61 ($V_2^{1'}$), 25 ($V_1^{1'}$)
	361.6	0.297	79 ($V_3^{1'}$), 8 ($V_2^{1'}$)	363.6	0.305	79 ($V_3^{1'}$), 8 ($V_2^{1'}$)	367.9	0.319	80 ($V_3^{1'}$), 8 ($V_2^{1'}$)
ACH_2^+(eq)	398.7	0.268	79 ($V_2^{1'}$), 9 ($V_3^{1'}$)	402.9	0.267	79 ($V_2^{1'}$), 8 ($V_3^{1'}$)	412.3	0.276	81 ($V_2^{1'}$), 7 ($V_3^{1'}$)
	391.6	0.258	90 ($V_1^{1'}$)	395.6	0.263	90 ($V_1^{1'}$)	403.9	0.281	90 ($V_1^{1'}$)
	339.2	0.299	75 ($V_3^{1'}$), 10 ($V_2^{1'}$)	341.4	0.301	75 ($V_3^{1'}$), 10 ($V_2^{1'}$)	346.4	0.300	76 ($V_3^{1'}$), 9 ($V_2^{1'}$)

All electron transitions are of $\pi \rightarrow \pi^*$ type.

and CI = 980 all the 35 occupied MO's and 15, respectively 28 unoccupied MO's were taken into account in CI. For ACH_2^+(eq) configuration interaction does not reflect the value of *f*, while for ACH_2^+ the taking into account of 980 monoexcited configurations leads to its considerable increase at the transition $S_0 \rightarrow S_1$ and decrease at the transition $S_0 \rightarrow S_2$. If 980 monoexcited configurations are taken into account, the electron transitions $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ for ACH_2^+(eq) fall into the region of the bands with maxima at λ = 401 and 354 nm, while for partial taking into account of the monoexcited configurations CI = 240, 525 these transitions are shifted to the shortest wavelength and do not pass into the region of these bands.

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