THE σ^* CONSTANTS OF IONIC SUBSTITUENTS

Ya. L. Yarv, T. I. Pekhk,
A. A. Aaviksaar, D. I. Lobanov,
and N. N. Godovikov

UDC 543.422.25:541.67:547.1'118

The presence of the kinetic salt effect in the alkaline hydrolysis reactions of organophosphorus compounds $[(C_2H_5O)(CH_3)P(O)S(CH_2)_m\overset{+}{S}(CH_3)C_2H_5]CH_3SO_4^-$ made it possible to obtain two sets of induction constants for the $(CH_2)_m\overset{+}{S}(CH_3)C_2H_5$ substituents, which corresponded to the rate constants at zero ionic strength ($\sigma^*_{\mu=0}$) and at high ionic strengths ($\sigma^*_{\mu\to\infty}$), where the rate constant is no longer dependent on the concentration of the added electrolyte [1]. In analyzing these σ^* constants it was shown that a constancy in the damping factor of the induction effect of the sulfonium group when m is increased is observed only when $\sigma^*_{\mu\to\infty}$. On this basis it was concluded that at low ionic strengths the interaction between the charged substituents and the reaction center is not uniform and, together with the induction effect, another effect, presumably the coulomb interaction of the ionic charges of the substituent and the reaction center in the activated state, contributes to the $\sigma^*_{\mu=0}$ constants. This effect becomes equal to zero at a high ionic strength. In such case it must be assumed that it is correct to use $\sigma^*_{\mu\to\infty}$ in the Taft equation for the σ^* constants of the charged substituents [1].

The results of a broader analysis of the kinetic data confirmed this conclusion [2, 3]. For a direct solution of this problem the σ^* constants for the charged substituents must be calculated by starting with processes where coulomb interaction between the charges of the substituents and the reaction center is excluded. Experimental data for the appropriate calculation are absent in the literature. In a number of cases it was shown that linear relationships are observed between the chemical shift of various nuclei and the induction constants [4, 5]. Consequently, in the present paper we determined the chemical shifts in the ^{31}P NMR spectra of the compounds $(C_2H_5O)_2P(O)SX$, where $X = (CH_2)_m\overset{+}{S}(CH_3)C_2H_5$ ($m = 2$–4, 6), $(CH_2)_mSC_2H_5$ ($m = 2$–4, 6), and C_nH_{2n+1} ($n = 6$, 8). The obtained δ_P values are given in Table 1. In Fig. 1 these data were compared with the induction constants, which were calculated by starting with the rate constants for the alkaline hydrolysis of the compounds $(C_2H_5O)(CH_3)P(O)SX$ with the same X substituents [1]. From Fig. 1 it can be seen that a general linear relationship is observed for the ionic and uncharged compounds when the $\sigma^*_{\mu\to\infty}$ values are used for the sulfonium substituents:

$$\delta_P = (28.85 \pm 0.06) - (2.60 \pm 0.06)\,\sigma^* \quad (\text{or} \quad \sigma^*_{\mu\to\infty}) \quad r = 0.999 \qquad (1)$$

The $\sigma^*_{\mu=0}$ constants have clearly high values, and their comparison with the δ_P values leads to a separate function, in which case the ordinate intercept, equal to 29.27 ± 0.09, is reliably different from the corresponding values for the nonionic compounds. This shows that the $\sigma^*_{\mu=0}$ constants cannot be considered within the framework of a single scale with the induction constants for the uncharged electronegative substituents.

As a result, the data based on the ^{31}P NMR spectra confirm the validity of selecting concentrated solutions of the electrolytes as the standard state for the experimental determination of the σ^* constants of ionic substituents. Here the salting out effect has to be taken into account when considering the rate of interionic reactions, which in a number of cases has a very substantial effect on the rate of the reactions.

EXPERIMENTAL

The synthesis and properties of the studied organophosphorus compounds were described previously [6]. The ^{31}P NMR spectra were taken on a universal spectrometer [7] at a frequency of 24.29 MHz, with noise decoupling from the protons; the external standard was 85% H_3PO_4. Freshly prepared solutions of the studied compounds in abs. ethanol were used.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Tartusk State University. Institute of Cybernetics, Academy of Sciences of the Estonian SSR, Tallin. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1649-1650, July, 1976. Original article submitted December 31, 1975.

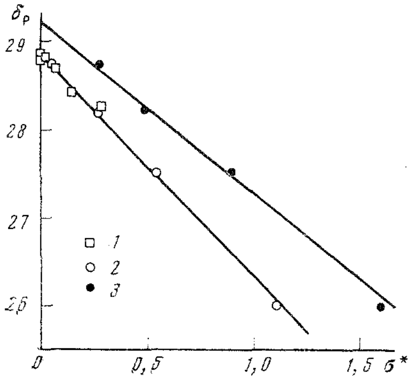

Fig. 1. Correlation of chemical shifts δ_P in ^{31}P NMR spectra of $(C_2H_5O)_2P(O)S(CH_2)_mSC_2H_5$ and $(C_2H_5O)_2P(O)SC_nH_{2n+1}$ with σ^* constants (1), and of compounds $[(C_2H_5O)_2P(O)S(CH_2)_m\overset{+}{S}(CH_3)C_2H_5]^- CH_3SO_4^-$ with $\sigma^*_{\mu\to\infty}$ (2) and $\sigma^*_{\mu=0}$ (3) constants.

TABLE 1. δ_P† Values of Compounds $(C_2H_5O)_2P(O)SX$

X	δ_P, ppm	σ^*	$\sigma^*_{\mu\to\infty}$	$\sigma^*_{\mu=0}$
$(CH_2)_2SC_2H_5$	28,24	0,28	—	—
$(CH_2)_3SC_2H_5$	28,42	0,14	—	—
$(CH_2)_4SC_2H_5$	28,66	0,07	—	—
$(CH_2)_6SC_2H_5$	28,82	0,017	—	—
$(CH_2)_2\overset{+}{S}(CH_3)C_2H_5$	25,99	—	1,10	1,60
$(CH_2)_3\overset{+}{S}(CH_3)C_2H_5$	27,51	—	0,55	0,91
$(CH_2)_4\overset{+}{S}(CH_3)C_2H_5$	28,20	—	0,27	0,49
$(CH_2)_6\overset{+}{S}(CH_3)C_2H_5$	28,72	—	0,06	0,28
C_6H_{13}	28,80	0	—	—
C_8H_{17}	28,84	0	—	—

---

†Relative to 85% H_3PO_4.

CONCLUSIONS

1. We determined the chemical shifts in the ^{31}P NMR spectra of the compounds $(C_2H_5O)_2P(O)SX$ ($X = (CH_2)_m\overset{+}{S}(CH_3)C_2H_5$, $(CH_2)_mSC_2H_5$ ($m = 2$-4 and 6)) and C_nH_{2n+1} ($n = 6, 8$), and obtained a linear correlation between δ_P and the σ^* constants of the X substituents.

2. The induction constants of the charged substituents, which were obtained from the rate of the interionic reactions at a high ionic strength of the medium, constitute a single scale with the σ^* constants for the uncharged electronegative substituents.

LITERATURE CITED

1. Ya. L. Yarv, A. A. Aaviksaar, N. N. Godovikov, and N. A. Morozova, Reakts. Sposobnost'Organ. Soedin., 9, 813 (1972).
2. V. A. Pal'm, V. M. Nummert, T. O. Pyussa, I. M. Karel'son, and I. A. Koppel, Reakts. Sposobnost' Organ. Soedin., 10, 223 (1973).
3. V. A. Pal'm, T. O. Pyussa, V. M. Nummert, and I. V. Tal'vik, Reakts. Sposobnost'Organ. Soedin., 10, 243 (1973).
4. S. H. Marcus and S. I. Miller, J. Phys. Chem., 68, 331 (1964).
5. V. E. Bel'skii, L. A. Kudryavtseva, and B. E. Ivanov, Zh. Obshch. Khim., 42, 2427 (1972).
6. Ya. L. Yarv, A. A. Aaviksaar, D. I. Lobanov, and N. N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., 426 (1976).
7. É. Lippmaa, T. Pekhk, and Ya. Past, Izv. Akad. Nauk ÉstonSSR, Ser. Tekhn. Fiz.-Mat. Nauk, 16, 345 (1967).