- 5. L. B. Volodarksii, L. N. Grigor'eva, and A. Ya. Tikhonov, Khim. Geterotsikl. Soedin., 1414 (1983).
- 6. L. Dogliotty and E. Hayon, K. Phys. Chem., 7], 2511 (1967).
- 7. R. Livingston and H. Zeldes, J. Chem. Phys., 44, 1245 (1966).
- 8. E. T. Denisov, Rate Constants for Homolytic Liquid-Phase Reactions [in Russian], Nauka, Moscow (1971).

EFFECT OF HIGH PRESSURE ON HYDROGEN ABSTRACTION BY THE CUMYLOXY RADICAL

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A quantitative relationship has been reported for volumetric activation effects (ΔV^{\neq}) and the reactivity of organic compounds in the transfer of hydrogen atoms to free radicals [1]. The formation of the transition state in these reactions is accompanied by a decrease in volume $(\Delta V^{\neq} < 0)$, i.e., the reaction is accelerated with increasing pressure, while the acceleration $(|\Delta V^{\neq}|)$ depends on the rate constants in accord with the empirical equation

 $(\Delta V_i^{\neq} - \Delta V_s^{\neq}) = \alpha \lg (k_i/k_s) \tag{1}$

where ΔV_{1}^{\neq} and ΔV_{5}^{\neq} are the volumetric activation effects of the i-th and a standard reaction, k_{1} and k_{s} are the rate constants of these reactions, and α is a constant.

The relative reactivity of C-H bonds of many hydrocarbons is a function of the dissocia-

tion energy of these bonds, i.e., the stability of the $\sum C'$ radicals formed. In this case,

the more rapid reactions are more strongly accelerated with increasing pressure ($\alpha < 0$ in Eq.

(1). This was observed in a study of hydrogen abstraction by polymer radicals $-\sum_{\ell}^{C} [2]$,

 $(CH_3)_3CO^{\circ}$ [3] and chlorine [4, 5] and bromine atoms [6]. In the present work, we studied the cumyloxy radical as a hydrogen acceptor.

Cumyloxy radicals were obtained by the homolysis of trimethylsilyl(cumyl)peroxide (TSCP) [7]. Upon the decomposition of TSCP in solution, the cumyloxy radicals formed undergo competing reactions: bimolecular reaction with the solvent RH (2) and a monomolecular reaction with loss of a methyl radical (3).

$$PhMe_{2}COOS_{1}Me_{3} \xrightarrow{k_{1}} PhMe_{2}CO \xrightarrow{} (DMPC)$$

$$(2)$$

$$(3)$$

$$(2)$$

$$(AP)$$

1 DU 2

This scheme implies that the ratio of the quantities of dimethylphenylcarbinol (DMPC) and acetophenone (AP) formed during the conversions depends on n (the number of hydrogen atoms susceptible to abstraction).

$$\frac{[\text{DMPC}]}{[\text{AP}]} = \frac{k_2}{k_3} [\text{RH}] n \tag{4}$$

Among the solvents used, anisole and toluene have three chemically equivalent hydrogen atoms (methyl group hydrogen atoms, n = 3); n = 9 for tert-butylbenzene and n = 1 for cumene since the hydrogen atom at the tertiary carbon atom is significantly more active than the other atoms. Analogously, only the number of hydrogen atoms bound to secondary carbon atoms was taken in the calculation for n-nonane (n = 14).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1205-1208, May, 1985. Original article submitted November 27, 1984. TABLE 1. Ratio of the Rate Constants for Hydrogen Atom Abstraction (k2) and β-Cleavage of the Cumyloxy Radical (k3) at High Pressures 1

ţ			Experim	ental valu	es			k ₂ / k ₃ (lit	ers/mole) at	different pre	ssures, MP/	A	$(\Delta V_3^{\neq} - \Delta V_3^{\neq})$
ЧХ	$(R_2/R_3)_0 *$	0,1	20	50	100	200	250	300	400	\$00	750	1000	°*. cm³/mole
Cumene 1-Nonane Anisole Foluene ert-Butylbenzene	0,105 0,014 0,011 0,015 0,0042	0,093	0,142 0,013 0,017 0,017	0,163 0,017 0,0043	0,167 0,025 0,022 0,023 0,023 0,023	0,28 - - 0,0077	0,44 0,029 0,030 0,040	0,47 	0,91 0,043 0,014	1,12 0,081 0,073 0,067 0,014	2,58 0,124 0,116 0,117 0,011 0,021	3,89 0,151 0,226 0,153 0,029 0,029 ***	$-27,1\pm4,1$ - $18,3\pm4,8$ - $24,7\pm4,0$ - $17,1\pm0,9$ - $17,1\pm0,9$ - $14,5\pm0,7$

*Calculated by the method of least squares from Eq. (5); the error corresponds to the 95% confidence level. †Data of our previous work [7]. ‡p = 900 MPa.

TABLE 2. Relative Reactivity of Solvents (k_1/k_S) on Difference in the Volumetric Activation Effects $(\Delta V_1^2-\Delta V_5^2)$, cm³/mole (s indicates the reaction of the cumyloxy radical with toluene)

			the second s	
		443 ° K	323 ° K	(calculated)
Solvent (i)	k2 /k8	$\langle \Delta V_{i}^{\neq} - \Delta V_{s}^{\neq} \rangle$	k_{i}/k_{s}	$(\Delta V_{\tilde{t}}^{\neq} - \Delta V_{B}^{\neq})$
	C L	G	2.2.4	अ
Cumene	0'2	21	14,4	0,0
Toluene	-	0	.	0
n-Noane	0,83	-1,2	0,77	-0,8
Anisole	0.73	-5,4	0,65	-3,1
tert-Butylbenzene	0,28	+2,6	0,17	+1,8

Table 1 gives the values for k_2/k_3 calculated using Eq. (4), the experimental [DMPC]/[AP] ratios, and the differences in the volumetric activation effects of reactions (2) and (3) calculated according to Eq. (5)

$$\lg (k_2/k_3)_p = \lg (k_2/k_3)_0 - \frac{(\Delta V_2^{\neq} - \Delta V_3^{\neq})_0}{T} \Phi$$
(5)

where $(k_2/k_3)_p$ and $(k_2/k_3)_o$ are the ratios of the reaction rate constants at pressure p and atmospheric pressure and Φ is a parameter characterizing the pressure calculated according to an equation proposed in our previous work [8].

We should note that the change in the k_2/k_3 ratio in different solvents and with increasing pressure is prmarily due to change in k_2 . According to Russel [9], the rate constant k_3 of the analogous reaction of the tert-butyloxy radical is virtually independent of the nature of the solvent. Marriott and Griller 10 have also reported that the β -cleavage reactions of radicals are only slightly inhibited with increasing pressure, i.e., have low positive volumetric activation effects from 0.2 to 3 cm³/mole. In addition, it is unlikely that the values for ΔV_3^2 will change markedly in the series of solvents studied.

Thus, by dividing the values of $(k_2/k_3)_0$ for different solvents by $(k_2/k_3)_0$ for toluene, we obtain a series of relative capacity of these compounds for hydrogen atom transfer to the cumyloxy radical, while by subtracting the corresponding value for toluene from differences $(\Delta V_2^2 - \Delta V_3^2)_0$ determined for different solvents, we obtain the difference in volumetric activation effects $(\Delta V_1^2 - \Delta V_5^2)$ (Table 2).

Comparison of these results with the data for the pressure effect on the analogous reactions of tert-butyloxy radicals [4] requires carrying out these reactions at 323°K as in our previous work [4].

As already noted, the relative reactivity of hydrocarbons in the abstraction of hydrogen atom from them by a free radical is a function of the difference in the dissociation energies of the C-H bonds, i.e., the differences in the activation energies. Hence, k_1/k_s for 323°K was calculated using the Arrhenius equation taking identical preexponential factors.

In order to convert $(\Delta V_1^{\neq} - \Delta V_5^{\neq})$ to 323°K, we used the linear temperature dependences of ΔV^{\neq} with the coefficient proposed by El'yanov [11] as a first approximation in calculations for nonionic reactions. The calculation results are given in Table 2, which indicates that the tertiary C-Hbond in cumene is the most reactive bond considered. The rate constant for the abstraction of this hydrogen atom is greater than the corresponding value for abstraction of a hydrogen atom from the primary carbon atom in tert-butylbenzene by a factor of 85. The difference in the volumetric activation effects for these reactions is -8.6 cm³/mole, i.e., the relatively fast reaction is more strongly accelerated by pressure. An increase in pressure from 0.1 to 1000 MPa leads to an acceleration of hydrogen abstraction from cumene by a factor of 40, while it leads to only a sevenfold acceleration for tert-butylbenzene.

The ratio of the rate constants for the transfer of a hydrogen atom from cumene and tertbutylbenzene to the tert-butyloxy radical is also 85 [4] and the difference in the volumetric activation effects (-7.1 cm³/mole) differs only by 1.5 cm³/mole.

Treatment of the dependence for $(\Delta V_1^{\neq} - \Delta V_5^{\neq})$ on $\log(k_1/k_s)$ (data in Table 2 at 323°K, except for the reaction with anisole) gives $\alpha = -4.7 \pm 0.4 \text{ cm}^3/\text{mole}$ (see Eq. (1)). The value $\alpha = -3.7 \text{ cm}^3/\text{mole}$ is found for tert-butyloxy radicals [4].

The point corresponding to anisole clearly falls off the line. Hence, the relative reactivity of anisole is a function not only of the C-H bond dissociation energy but also polar factors. In our previous work [12, 13], we studied the effect of pressure on hydrogen abstraction by a bromine atom from the meta and para positions of toluene. The relative reactivity of these positions decreases with increasing electron-withdrawing capacity of the substituent. The dependence for $(\Delta V_1^{\neq} - \Delta V_5^{\neq})$ on $\log(k_i/k_s)$ in this case is also linear, but the coefficient α in Eq. (1) has a positive value, i.e., relatively slow reactions are more strongly accelerated with increasing pressure.

We may consider that the rate constant for hydrogen atom abstraction by electrophilic cumyloxy radical also decreases as a result of the inductive effect of the oxygen atom, while the negative volumetric activation effect increases. This is in accord with the activity found for anisole in this reaction.

EXPERIMENTAL

The experiments were carried out in a cylinder-piston unit according to our previous [7] technique. The products were analyzed by gas-liquid chromatography on a Biokhrom-1 chromatograph using a 100 × 0.3 cm glass column packed with 3% OV-1 on Super Chromaton (0.101-0.16 mm), with temperature rise from 323 to 473°K at 2 deg/min, 40 ml/min nitrogen carrier gas velocity, and dodecane as internal standard.

CONCLUSIONS

1. A quantitative dependence was found for the volumetric activation effect on the reactivity of cumene, n-nonane, toluene, and tert-butylbenzene for hydrogen atom transfer to the cumyloxy radical.

2. The analogous reaction of the cumyloxy radical with anisole does not obey this relationship since the reactivity of anisole is apparently a function not only of the C-H bond dissociation energy but also polar factors.

LITERATURE CITED

- 1. V. M. Zhulin, Rev. Phys. Chem. Jpn., <u>50</u>, 217 (1980).
- 2. V. M. Zhulin, Izv. Akad. Nauk SSSR, Ser. Khim., 2361 (1971).
- 3. V. M. Zhulin and B. I. Rubinshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 2201 (1976).
- 4. V. M. Zhulin and B. I. Rubinshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 478 (1977).
- 5. V. M. Zhulin, B. I. Rubinshtein, and M. Ya. Botnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 293 (1975).
- V. M. Zhulin, M. Ya. Botnikov, and I. Kh. Milyavskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1131 (1975).
- V. M. Zhulin, G. A. Stashina, A. V. Ganyushkin, N. V. Yablokova, V. A. Yablokov, and O. B. Rudakov, Izv. Akad. Nauk SSSR, Ser. Khim., 1659 (1983).
- 8. E. M. Vasil'vitskaya, B. S. Él'yanov, and V. M. Zhulin, Izv. Akad. Nauk SSSR, Ser. Khim., 2607 (1984).
- 9. G. Russel, J. Org. Chem., 24, 300 (1959).
- 10. P. R. Marriott and D. Griller, J. Am. Chem. Soc., <u>103</u>, 1521 (1981).
- 11. B. S. Él'yanov and E. M. Vasylvitskaya (Vasil'vitskaya), Rev. Phys. Chem. Jpn., <u>50</u>, 169 (1980).
- V. M. Zhulin, M. Ya. Botnikov, and I. Kh. Milyavskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 488 (1975).
- M. Ya. Botnikov, I. Kh. Milyavskaya, and V. M. Zhulin, Izv. Akad. Nauk SSSR, Ser. Khim., 577 (1977).