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Effect of the Medium on the Reaction of *tert*-Butyl Hypochlorite with Hydrocarbons

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Abstract—The selectivity in the reaction of *tert*-butyl hypochlorite with 2,3-dimethylbutane in various solvents may be described by a three-parameter correlation equation taking into account the ability of solvents to nonspecific solvation and their cohesion energy density.
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Despite generally accepted views implying insignificance of solvent effect on the rate of homolytic reactions, experimental data suggest that the rate of such processes can change even over several orders of magnitude depending on the solvent properties. Proper relations between the rate constants of some reactions involving decomposition of peroxy [1] and azo compounds [2], as well as of radical oxidation processes [3], and physical parameters of solvents were derived on the basis of multiparameter linear equations based on the linear free energy relations unlike heterolytic processes, not only solvation parameters but also self-association of the medium (which defines so-called cage effect) are significant in this case.

We have recently revealed [4] that such an approach is also effective for description of data [5] on the selectivity of photochemical chlorination of 2,3-dimethylhexane. The ratio of the tertiary and primary replacement products (Q), which is determined by the ratio of the rates of the corresponding processes, is satisfactorily described by six-parameter linear Eq. (1) (the multiple correlation coefficient R is 0.962) for 23 solvents:

$$Q = a_0 + a_1\frac{n^2-1}{n^2+2} + a_2\frac{\varepsilon-1}{2\varepsilon+1} + a_3B + a_4E_T + a_5\delta^2 + a_6V_m. \quad (1)$$

Here, n and ε are, respectively, the refractive index and dielectric constant of solvents, which reflect their polarizability and polarity responsible for nonspecific solvation of reagents or reaction complex; B is the basicity according to Palm [6], and E_T is the electrophilicity according to Reichardt [7] (these parameters determine the ability of a solvent to possible specific, e.g., acid–base, interactions); and the squared Hildebrand solubility parameter δ^2 and the molar volume V_m characterize structural specificity of the medium. In the given case, the most significant is polarizability factor [the pair correlation coefficient r between Q and $f(n^2)$ is equal to 0.867]; however, the parameters $f(\varepsilon)$ and shop; V_m are to be taken into account to obtain an appropriate correlation. The parameters B and E_T are insignificant, indicating the absence of acid–base interaction. The effect of self-association is also insignificant.

It was interesting to check whether Eq. (1) can be applied to generalize data of other studies on the effect of the medium on the product ratio, i.e., on the rates of two alternative radical processes. Walling and Wagner [8] studied the reaction of 2,3-dimethylbutane (I, 0.8 M) with *tert*-butyl hypochlorite (0.2 M) in 16 solvents in the temperature range from 0 to 100°C under UV initiation. It is known that *tert*-butyl hypochlorite under UV irradiation decomposes to generate $(CH_3)_3CO^{\cdot}$ radicals and that the latter are capable of either undergoing rearrangement with elimination of methyl radical or reacting with other compounds (in the given case, with hydrocarbons).

$$(CH_3)_3CO^{\cdot} + RH \xrightarrow{k_a} (CH_3)_3COH + R^{\cdot}, \quad (2)$$

$$(CH_3)_3CO^{\cdot} + RH \xrightarrow{k_d} CH_3COCH_3 + CH_3^{\cdot}. \quad (3)$$

Table 1. Ratios of the yields of 2-chloro-2,3-dimethylbutane and 1-chloro-2,3-dimethylbutane Q in different solvents at 0, 25, 40, 70°C [8]

Solvent no.	Solvent	0°C	25°C			40°C	75°C	$E_p - E_t$, kcal mol^{-1}
			exptl.	calcd.	ΔQ			
1	Anisole	106	72.0	68.3	–3.7	65	45	2.25
2	Bromobenzene	104	78.0	80.8	2.8	64	47	2.13
3	*tert*-Butylbenzene	96	75.0	63.7	–11.3	63	44	2.05
4	Benzene	89	70.0	75.7	5.7	55	–	1.99
5	*trans*-Dichloroethylene	75	61.0	63.2	2.2	50	40	1.74
6	*cis*-Dichloroethylene	60	47.0	42.0	–5.0	40	29	1.89
7	Chlorobenzene	94	66.0	65.4	–0.6	54	35	2.58
8	*o*-Dichlorobenzene	91	66.0	71.2	5.2	50	34	2.63
9	Benzonitrile	67	48.0	–	–	40	25	2.57
10	*tert*-Butyl alcohol	–	38.0	36.7	–1.3	30	20	3.06
11	Acetone	128	76.0	–	–	51	30	3.77
12	Acetonitrile	–	47.0	40.8	–6.2	33	17	4.57
13	Acetic acid	53	28.0	35.0	7.0	20	–	4.21
14	Methyl acetate	25	17.0	22.3	5.3	14	10	2.35

The chlorination of 2,3-dimethylbutane (**I**) leads to the formation of tertiary and primary products, 2-chloro-2,3-dimethylbutane (**II**) and 1-chloro-2,3-dimethylbutane (**III**), respectively, whose ratio is determined by the corresponding rate constants k_t and k_p. Depending on the solvent nature, the ratio $Q = k_t/k_p$ may change approximately by a factor of 4; for instance, it is 17 in methyl acetate and 72 in anisole at 25°C.

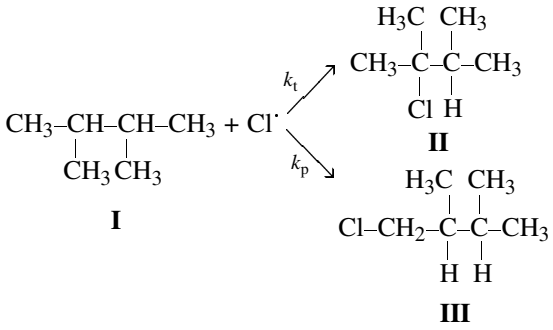

Table 1 contains the ratios k_t/k_p at 0, 25, 40, and 70°C, as well as the differences in the activation energies of the two processes ($E_p - E_t$, kcal mol^{-1}), taken from [8]. Insofar as the ratio Q at 100°C was determined only in a few solvents, the corresponding data are not given. The reaction at 25 and 40°C was studied in all the examined solvents (N = 16); however, the data obtained in 80% acetone and in the absence of a solvent (neat 2,3-dimethylbutane) [8] were also excluded.

In keeping with the linear free energy relationship, the change in the free energy during a process is proportional to the logarithm of the rate constant. Correspondingly, treatment of the data in Table 1 [$\log Q = \log(k_t/k_p)$] for 14 solvents at 25°C according to Eq. (1) gives an expression with a multiple correlation coefficient R of 0.672. Exclusion of the most strongly deviating data for acetone and methyl acetate gives R = 0.951 for the 12 remaining solvents. As we showed in [4], data on the effect of the medium on the ratio of two products in the photochemical chlorination of 2,3-dimethylbutane are described better using the values of Q rather than $\log Q$. In this case, generalization of the data obtained at 25°C in 14 solvents gave a correlation with an unsatisfactorily poor multiple correlation coefficient, R = 0.704; successive exclusion (according to the IUPAC recommendations [9]) of the most strongly deviating data for acetone and benzonitrile allowed us to raise R to 0.929 and 0.977, respectively [Eq. (4)]:

$$Q = -75.86 + (330.5 \pm 67.4)f(n^2) - (144.7 \pm 28.6)f(\varepsilon) - (0.03 \pm 0.03)B - (0.18 \pm 0.46)E_T + (0.20 \pm 0.03)\delta^2 + (0.23 \pm 0.09)V_m, \quad (4)$$
$$N\ 12;\ R\ 0.977;\ s\ \pm 4.26.$$

Hereinafter, a good quality of the obtained correlation follows from the agreement between the Fisher consistency calculated for a confidence probability α of 0.95 and the reference value for the corresponding number of points. It should be noted that no reliable correlation was found in [10] while treating the log (k_t/k_p) values given in [8] according to the Koppel–Palm equation and that the use of Swain's

equation [11] for 9 solvents led to an R value of 0.898 (the determining factor was solvent acidity).

The pair correlation coefficients r between Q and particular parameters (after exclusion of deviating data) are 0.872, 0.490, 0.596, 0.718, 0.328, and 0.647, respectively. Though these values indicate possible prevalence of the polarizability and electrophilicity factors, their significance cannot be estimated. Therefore, following the procedure described in [9], the significance of a particular parameter was estimated by successive exclusion of one parameter and calculation of R for each correlation with a lower number of terms thus obtained. In such a way we found low significance of the specific nucleophilic solvation (B) and molar volume (V_m) factors; exclusion of B reduces R only to 0.974, while the subsequent exclusion of V_m gives a four-parameter equation with $R = 0.962$.

$$Q = -55.71 + (422.8 \pm 58.7)f(n^2) - (127.6 \pm 35.1)f(\varepsilon) + (0.16 \pm 0.04)\delta^2 - (0.58 \pm 0.55)E_T, \quad (5)$$
$$R\ 0.962;\ s\ \pm 5.42.$$

The electrophilicity factor E_T is also characterized by a low significance; thus, the relation between the ratio of the tertiary and primary chlorination products can be described satisfactorily by three-parameter Eq. (6).

$$Q = -81.67 + (460.5 \pm 48.7)f(n^2) - (144.6 \pm 32.5)f(\varepsilon) + (0.16 \pm 0.04)\delta^2, \quad (6)$$
$$R\ 0.958;\ s\ \pm 5.68.$$

Further exclusion of any term from Eq. (6) impairs the correlation to R values lower than 0.90; the results are most sensitive to the polarizability parameter. As in the photochemical chlorination of compound **I** [4], the isomer ratio Q is determined mainly by nonspecific solvation of the substrate, which is related to the polarizability of a solvent: the pair correlation coefficients between Q and $f(n^2)$ at 25°C are 0.887 [4] and 0.872, respectively. In both cases, insignificance of possible specific interactions should be noted. On the other hand, the two other factors, $f(\varepsilon)$ and V_m in the first case and $f(\varepsilon)$ and δ^2 in the second, produce only correctional effect: exclusion of $f(n^2)$ from the three-parameter equation reduces R to ~0.6 (i.e., correlation is lacking), whereas exclusion of $f(\varepsilon)$, V_m, or δ^2 leads to a two-parameter equation with an R value ranging from 0.90 to 0.94.

It is important that, in both cases (photochemical chlorination of **I** [4] with chlorine and reaction with *t*-BuOCl), the Hildebrand solubility parameter δ^2 is included with the "plus" sign, for self-association is responsible for the cage effect which favors radical reactions.

Table 1 contains Q values calculated by Eq. (6) and deviations ΔQ of the calculated from experimental values. The differences ΔQ are comparable with the root-mean-square error $s = \pm 5.68$, or they insignificantly exceed the latter. The ΔQ values for the excluded solvents (benzonitrile and acetone) and excess dimethylbutane (no solvent; the data are not given in Table 1) are much greater.

Analogous relations were found when the data at 0, 40, and 70°C [8] were generalized using Eq. (1). The corresponding experimental data are also given in Table 1. It is seen that the probability for chlorination at the tertiary carbon atom increases as the temperature decreases: the Q value is 50–100 at 10°C, 10–50 at 70°C, and 10–20 at 100°C. The temperature dependence of Q is almost linear (Fig. 1), while in some cases only a tendency is observed. Probably, this is the reason that the data for acetone do not fit the correlation. The slope of the $Q = f(T)$ straight lines depends on the difference in energies of activation of both processes ($E_t - E_p$). The reciprocal temperature dependences $Q = f(1/T)$ are mostly curvilinear.

Equations (4) and (5) for 0, 40, and 70°C are analogous to those derived from the data obtained at 25°C. The multiple correlation coefficients R range from 0.6 to 0.8 for 12 solvents; exclusion of the data for acetone leads to an acceptable R value of more than 0.95. The R value does not decrease to a considerable extent upon removal of the B and V_m terms. The determining factor is polarizability $f(n^2)$. Some deviations are observed only for the data obtained at 40°C.

The difference in the activation energies $E_p - E_t$ can also be described using a multiparameter equation. The multiple correlation coefficient for all 14 solvents is equal to 0.878; exclusion of the data for *cis*-dichloroethylene and methyl acetate leads to satisfactory correlation (7):

$$E_p - E_t = 2.08 - (14.6 \pm 3.7)f(n^2) + (3.8 \pm 1.6)f(\varepsilon) - (3.8 \pm 1.8)B + (75.7 \pm 26.1)E_T + (0.83 \pm 1.82)\delta^2 + (4.3 \pm 5.0)V_m, \quad (7)$$
$$N\ 12;\ R\ 0.965;\ s\ \pm 0.2.$$

Here, the significance of the B, δ^2, and V_m parameters is small, and an acceptable accuracy is achieved with three-parameter Eq. (8):

$$E_p - E_t = 1.56 - (9.52 \pm 2.94)f(n^2) + (2.69 \pm 1.33)f(\varepsilon) + (0.07 \pm 0.03)E_T, \quad (8)$$
$$R\ 0.949;\ s\ \pm 0.29.$$

Insofar as the $Q = k_t/k_p$ and $\Delta E = E_p - E_t$ values are given in [8] and hence in Table 1, the signs at the

Table 2. Ratios of the yields of acetone and *tert*-butyl alcohols in different solvents at 0, 25, 40, 70, and 100°C [8]

Solvent no.	Solvent	0°C	25°C			40°C	70°C	100°C	$E_d - E_a$, kcal mol^{-1}
			exp.	calc.	ΔQ				
1	Acetonitrile	81.9	19.8	21.1	1.3	8.1	2.3	0.7	9.54
2	Benzene	207.0	48.6	–	–	24.7	7.6	2.8	8.66
3	*m*-Dichlorobenzene	178.0	45.7	47.9	2.2	24.3	7.1	2.8	8.40
4	Bromobenzene	162.0	45.2	49.6	4.4	25.4	7.3	2.9	8.17
5	*o*-Dichlorobenzene	120.0	35.2	33.0	–2.2	19.2	5.8	2.2	8.14
6	Benzonitrile	109.0	33.4	30.2	–3.2	16.9	4.9	1.9	8.28
7	Fluorobenzene	127.0	43.4	33.4	–10.0	22.4	6.9	2.7	7.85
8	Chlorobenzene	91.7	28.6	37.0	8.4	16.4	5.6	2.7	7.21
9	Acetic acid	12.6	4.9	5.0	0.1	2.9	1.3	0.7	5.95
10	Tetrachloroethylene	293.0	87.8	82.7	–5.1	39.0	11.1	4.1	8.72
11	1,1-Dichloroethylene	75.7	24.6	34.0	9.4	14.2	4.9	2.0	7.34
12	*cis*-Dichloroethylene	52.2	16.9	11.5	–5.4	9.1	3.7	1.6	7.04
13	*trans*-Dichloroethylene	98.9	33.0	–	–	14.2	5.6	2.3	7.69

corresponding terms in the equations for Q and ΔE are opposite.

Walling and Wagner [8] also measured the product ratios in the reaction of *tert*-butoxy radical with 2,3-dimethylbutane in the presence of excess cyclohexane (5 : 1). The reaction follows schemes (2) and (3) and yields *tert*-butyl alcohol and acetone. The product ratios $Q = k_a/k_d$ in different solvents in the temperature range from 0 to 100°C and the differences in the activation energies $E_d - E_a$ are given in Table 2. The product ratios (k_a/k_d) are satisfactorily described by multiparameter equations. The data for *trans*-dichloroethylene fall out from these correlations, and they were not included (and are not given in Table 2). Analysis of six-parameter Eq. (1) revealed insignificance of the solvent basicity (B) and polarizability factors. On the other hand, the ability to electrophilic solvation is relatively significant.

The R value for 12 solvents is 0.900 (25°C); after exclusion of the data for benzene, an acceptable correlation with $R = 0.962$ is obtained, and the coefficient R almost does not decrease upon elimination of the low-significant solvent basicity and polarizability factors.

$$Q = 95.50 - (274.69 \pm 48.54)f(\varepsilon) - (1.66 \pm 0.69)E_T + (0.198 \pm 0.042)\delta^2 + (0.31 \pm 0.15)V_m, \quad (9)$$
$$R\ 0.961;\ s\ \pm 5.98.$$

Analogous correlations were derived from the data obtained at other temperatures; there was no necessity of excluding data for some solvents to achieve acceptable R values. The regression coefficients considerably change with rise in temperature; the root-mean-square deviations s change correspondingly. Further analysis showed relatively low significance of the E_T parameter: after exclusion of the E_T term, the R value decreases to 0.940–0.950. Removal of V_m reduces R to 0.920–0.940, while the multiple correlation coefficient R becomes smaller than 0.9 upon exclusion of either δ^2 or $f(\varepsilon)$; therefore, the latter contribute most to the reaction selectivity Q. Here, it should be noted that, unlike the chlorination of dimethylbutane with chlorine (Fig. 1), the temperature dependences of Q for the reaction of *tert*-butoxy radical with 2,3-dimethylbutane are curvilinear (Fig. 2).

Analysis of the above correlations shows that the ability of solvents to undergo self-association favors reaction of $(CH_3)_3CO^{\cdot}$ radicals with excess cyclo-

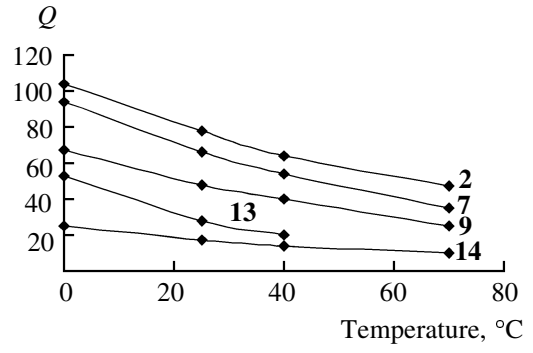

Fig. 1. Plots of the ratio of 2-chloro-2,3-dimethylbutane and 1-chloro-2,3-dimethylbutane versus temperature (the numbers of curves correspond to the numbers of solvents in Table 1).

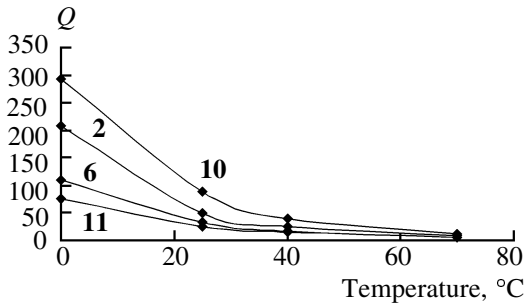

Fig. 2. Plots of the ratio of acetone and *tert*-butyl alcohol (the numbers of curves correspond to the numbers of solvents in Table 2).

hexane, presumably as a result of cage effect; increase of the molar volume produces a weaker effect. On the other hand, nonspecific [$f(\varepsilon)$] or specific (E_T) solvation of $(CH_3)_3CO^{\cdot}$ radicals favors dissociation of the latter. By contrast, the data on photochemical bromination of a mixture of cyclopropylbenzene and toluene in organic solvents [12] indicate that increase in δ^2 and V_m favors opening of the three-membered ring and that rise in polarity increases the yield of benzyl bromide [4].

The revealed insignificance of the solvent basicity B (the ability to nucleophilic solvation) is consistent with the qualitative conclusion drawn in [8] that the contribution of charge transfer in the transition state upon hydrogen abstraction by alkoxyl radical is small, for the maximal difference in the selectivity is observed in polar media (aromatic solvents are characterized by a considerably weaker effect). Our results disprove Russel's assumption implying possible influence of complex formation between the chlorine atom and π-electron system of the aromatic ring [5]. Walling and Wagner [8] also presumed possible effects of solvent polarity and polarizability, but only qualitative correlations of Q with the dielectric constant ε, dipole moment μ, and Kosower polarity parameter Z were obtained. On the one hand, our results confirm the determining role of nonspecific solvation in the process under study; on the other hand, they rationalize the lack of a distinct relation: Quantitative generalization of the influence of solvent properties on the selectivity may be achieved only with the aid of multiparameter equations taking into account joint effect of different factors. It should also be noted that the Kosower parameter Z reflects the electrophilicity rather than polarity, for it is proportional to the Reichardt parameter E_T [13].

The lack of satisfactory correlation between the selectivity of radical bromination and particular solvent parameters, specifically their polarity, was also shown in [12]. However, the cohesive energy density (internal pressure) proposed by the authors as an optimal parameter gave only rough consistency; as we showed in [4], the application of multiparameter equations is more appropriate in this case as well.

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