carried out on a layer of silica gel containing 10% moisture, its specification and preparation have been given in [17]. Eluant: methanol/chloroform 1:10. The spots of the tetraalkyl(aryl)-methylenediphosphine dioxide were made visible by iodine vapor. The Rf values are given in Table 2.

Determination of the basicity of the tetraalkyl-(aryl)-methylenediphosphine oxides was carried out by potentiometric titration in nitromethane with glass and aqueous calomel electrodes with negligible current flow; the initial concentration of the compounds in the titration solutions was 1.25 x 10^{-3} M, titrant of 0.125 M solution of HClO₄ in nitromethane. Details of the method of determining pK have been described previously [7].

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RELATIONSHIP BETWEEN UNPAIRED ELECTRON DENSITY AND REACTIVITY IN RADICALS

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It is known that the chemical activity of radicals with a localized valence is greater than the activity of groups in which the unpaired electron is delocalized over a system of conjugated bonds. N. N. Semenov links the decrease in activity of such groups to an increase in the conjugation energy [1]. A similar approach was employed by Kh. S. Bagdasaryan [2] in the analysis of the reactivity of radicals participating in polymerization and copolymerization processes.

An attempt is made in the present work to apply another criterion to the explanation of a different reactivity of radicals with conjugated bonds. It is based on a comparison of the density of the unpaired electron in the reaction center of the radical with the reactivity of the latter.

As basis for the link between unpaired electron density and reactivity of radicals, one may use the Polanyi-Semenov relation for the dependence between heat effects and activation energies for the reactions of these radicals. Let us choose some standard reaction of different radicals with the same molecule:

\[ R_1 + R'X \rightarrow R_1X + R' + \Delta Q_1 \]
\[ R_2 + R'X \rightarrow R_2X + R' + \Delta Q_2 \]
The heat effects of these reactions differ from each other by the difference in the energies of the bonds $R_1X$, $R_2X$, etc., since the broken $R'X$ bond is the same. Consequently, the dependence of the heat effect involved in the reaction of radical $R_i$ with a molecule on the density of the unpaired electron must in many cases correspond to the dependence of the $R_iX$-bond energy on the density of the unpaired electron at the carbon atom participating in that bond.

Figure 1 shows the dependence of the breaking energy of the bonds in the compounds $CH_3-CH_3$, $CH_2=CHCH_2-CH_2CH=CH_2$, $C_6H_5CH_2-CH_2C_6H_5$, $C_6H_5CH_2-CH_2C_6H_5$, $C_6H_5C-C(C_6H_5)CH_3$ on the density of the unpaired electron at the $C$ atom, calculated according to the Hückel molecular orbital ($\alpha e$) method [3] in the radicals $CH_3$, $CH_2=CHCH_2$, $C_6H_5CH_2$, $C_6H_5CH_2$, $C_6H_5C-C(C_6H_5)C$. It is seen that $D_{R_1-R_i}$ depends linearly on $\alpha e$. The equation expressing this dependence has the form

$$D_{R_1-R_i} = 89.31\alpha e - 5.92.$$  \[1\]

Figure 2 shows the dependences of $D_{R_1-X}$ on $\alpha e$ for $X = CH_3$, $H$, $Cl$, $Br$, and $I$. These relationships are likewise described by equations of the form

$$D_{R_1-X} \approx k_0 + b,$$  \[2\]

where $k$ is equal to 40.79 ($CH_3$), 42.22 ($H$), 44.0 ($Cl$), 39.12 ($Br$), and 39.36 ($I$), respectively. The value of $k$ is changed slightly as $X$ is changed, whereas $b$ depends essentially on the nature of $X$ and is equal to 41.02 ($CH_3$), 57.0 ($H$), 37.72 ($Cl$), 26.35 ($Br$), and 14.57 ($I$), respectively. The parameters for Eqs. (1) and (2) are obtained by the least-squares method and are expressed in kcal/mole, whereas the bond energies are taken from [4, 5]. In view of the fact that many bond energies are given in the literature without any indication of the error in the measurements, in the evaluation of the parameters in Eqs. (1) and (2) these errors were not taken into account. In Eq. (1) the angular coefficient is close to the bond energy in ethane (83 kcal/mole), whereas in Eq. (2) it can in first approximation be regarded as constant and equal to one half of this value (41.5 kcal/mole). Equation (2) in the form

$$D_{R_1-X} \approx Q_{CH_3}e + Q_x,$$  \[3\]

where $Q_{CH_3} = 41.5$ kcal/mole reflects a certain additivity of bond energies.

Starting from this formula, we can write expressions for the activation energy ($E_i$) of reaction (1) for radicals $R_i$ with the molecule $R'X$:

$$E_i = A - \alpha |\Delta Q_i| \approx A - \alpha |Q_{CH_3}e + Q_x - D_{R'X}| = A + \alpha D_{R'X} - \alpha Q_x - \alpha Q_{CH_3}e = B - \alpha Q_{CH_3}e.$$

According to the data of Semenov [1], the mean value $\alpha = 0.25$. Then $\alpha Q_{CH_3} = 10$ kcal/mole. In this