

**EFFECT OF MEDIUM ON ELECTRONIC SPECTRA  
OF 4-DIMETHYLAMINO- $\omega$ -NITROSTYRENES.  
EFFECTIVE KIRKWOOD-ONSAGER FUNCTIONS OF MEDIUM**

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Wavenumbers of the longest-wave maxima of 1-nitro-2-(4'-dimethylaminophenyl)ethene and 2-nitro-1-(4'-dimethylaminophenyl)propene have been measured in 60 aprotic solvents. The values obtained along with the published data on the effect of medium on electronic spectra of eight other indicators (also measured in gas phase) have been used to suggest effective Kirkwood-Onsager functions for characterization of the overall polarizability of medium, inclusive of the gas phase, in the sense of the method of the product term. Applicability of these functions has been tested for evaluation of the effect of medium on electronic and infrared spectra, reaction rates and equilibria. The effect of medium on the rate of the Menshutkin reactions is interpreted as a consequence of the influence on the fast process ( $10^{13} \text{ s}^{-1}$ ) in the complex formed from the reactants.

The attempts at elaboration of a reliable empirical method for universal evaluation of the effect of medium on chemical and physical processes and properties take two paths at present. The first one starts from a study of the medium effect on some property (most frequently spectral) of the indicator chosen or of several indicators, and the constructed scale or scales of the medium characteristics are confronted with experimental data about the effect of medium on some other properties and processes. In this respect the most important results are those by Kamlet and Taft<sup>1</sup> and Reichardt<sup>2</sup>. The other path starts from the highest possible number of experimental data on the effect of medium on various properties from spectral region or from region of chemical reactivity and statistically searches parameters for each medium which satisfy best the chosen set of the properties considered. In this respect the most significant works are those by Pytela<sup>3</sup>, Chastrette<sup>4</sup>, and Sjöström and Wold<sup>5</sup>. Both the approaches show that a general evaluation of the medium effect necessitates four parameters which are usually interpreted (although not always in an open way) as the effects of polarity, polarizability, acidity, and basicity of medium. Mutual correlations between the individual parameters show that the basicity and acidity characteristics obtained by different ways stand in satisfactory relations and lead to reliable predictions of the medium effect. However, the polarity and polarizability characteristics appear to be rather vague, and their intercorrelations sometimes are not quite convincing.

The aim of the present study is an evaluation of the medium effect on electronic spectra of 1-nitro-2-(4'-dimethylaminophenyl)ethene (*I*) and 2-nitro-1-(4'-dimethylaminophenyl)-1-propene (*II*) and, in the sense of the method of the product term<sup>6,7</sup>, a suggestion and testing of the effective Kirkwood–Onsager characteristics of the overall polarizability of medium within the range also including the gas phase.

### EXPERIMENTAL

1-Nitro-2-(4'-dimethylaminophenyl)ethene (*I*) and 2-nitro-1-(4'-dimethylaminophenyl)-1-propene (*II*) were prepared by condensation of N,N-dimethylaminobenzaldehyde with nitromethane and nitroethane, respectively, according to Drain and Wilson<sup>8</sup>. The identity and purity of the samples prepared were checked by their melting points, elemental analyses, and NMR spectra. The solvents used were dried, distilled or rectified, and kept over the molecular sieve Nalsit 4. The electron spectra were measured with a Unicam SP 1800 spectrometer.

### RESULTS AND DISCUSSION

The electronic spectrum of 1-nitro-2-(4'-dimethylaminophenyl)ethene (*I*) shows two intensive absorption bands about 400 and 260 nm and two bands of low intensity about 312 and 326 nm. The assignment of these bands was carried out by means of the PPP-SCF-MO-CI method<sup>9</sup>. The longest-wave absorption band corresponds to the  $\pi-\pi^*$  transition connected with an intramolecular charge transfer from aromatic ring to nitro group, the position of this band being strongly dependent on medium. The same transition of 2-nitro-1-(4'-dimethylaminophenyl)-1-propene (*II*) has only slightly higher energy demands. The results of measurements of the medium effect on positions of maxima of these bands are given in Table I. For 37 aliphatic aprotic solvents from the studied set we evaluated the medium effect by means of the function of relative permittivity ( $D$ ) and refractive index ( $n$ ):  $f(D) = (D - 1)/(2D + 1)$  and  $f(n^2) = (n^2 - 1)/(2n^2 + 1)$  using the method of the product term<sup>10,11</sup>:

$$\tilde{\nu} = A + B \cdot f(D, n^2) + C \cdot f(n^2). \quad (1)$$

In Eq. (1) it is  $f(D, n^2) = f(D) \cdot f(n^2)$ ,  $B$  and  $C$  are the regression coefficients, and the absolute term  $A$  has the meaning of the wavenumber of the transition of the compound measured in gas phase. For the nitrostyrenes studied this relation was expressed by Eqs (2) and (3) (the wavenumbers are given in  $\text{cm}^{-1} \cdot 10^{-3}$ ).

$$\tilde{\nu} = 27.55 - 51.3f(D, n^2) - 1.4f(n^2) \quad R = 0.983, \sigma = 0.22 \quad (2)$$

$$\tilde{\nu} = 28.50 - 44.7f(D, n^2) - 5.1f(n^2) \quad R = 0.992, \sigma = 0.14 \quad (3)$$

$R$  means the correlation coefficient and  $\sigma$  is standard deviation. From Eq. (2) it is obvious that the medium-induced changes in the position of the absorption maximum

TABLE I

Effect of medium on position of absorption maxima (nm) in electronic spectra of  $\omega$ -nitrostyrenes I and II and the  $W$  and  $W \cdot f(n^2)$  characteristics of solvents

Solvent	$W$	$f(n^2)$	$W \cdot f(n^2)$	$\lambda_I$	$\lambda_{II}$
Gaseous state	0.000	0.000	0.0000	—	—
Perfluorohexane	0.131	0.134	0.0176	376.5	370.5
Perfluoroheptane	0.164	0.140	0.0230	—	—
Perfluorooctane	0.146	0.145	0.0212	—	—
Perfluorodimethyldecaline	0.153	0.162	0.0248	—	—
Pentane	0.183	0.180	0.0329	390	384
Hexane	0.193	0.185	0.0357	391.5	385
Heptane	0.199	0.191	0.0380	393	387.5
Isooctane	0.178	0.192	0.0341	392.5	386
Nonane	0.203	0.197	0.0400	—	—
Decane	0.197	0.199	0.0384	—	—
Cyclopentane	0.193	0.197	0.0380	395.5	389
Cyclohexane	0.193	0.204	0.0393	396.5	391
Methylcyclohexane	0.202	0.204	0.0412	—	—
Tetrachloromethane	0.242	0.216	0.0523	407.5	399
Trichloromethane	0.414	0.209	0.0828	440.5	426
Dichloromethane	0.435	0.202	0.0879	441.5	426.5
Tetrachloroethylene	0.222	0.230	0.0511	408	401
Trichloroethylene	0.313	0.221	0.0692	424	412
<i>trans</i> -Dichloroethylene	0.308	0.210	0.0647	—	—
1,2-Dichloroethane	0.445	0.200	0.0890	441	426.5
1,1,2-Tetrachloroethane	0.437	0.225	0.0983	453.5	436
1,1,1-Trichloroethane	0.342	0.208	0.0712	—	—
1,1,2-Trichloroethane	0.441	0.209	0.0921	—	—
Pentachloroethane	0.322	0.229	0.0737	—	—
Dibromomethane	0.390	0.239	0.0932	450	434.5
Tribromomethane	0.370	0.254	0.0940	450	436
Ethyl bromide	0.365	0.205	0.0748	428	416
1,2-Dibromoethane	0.346	0.239	0.0827	441	420
Diiodomethane	0.359	0.287	0.1030	462	447
Ethyl iodide	0.343	0.231	0.0792	433.5	416
Benzene	0.309	0.227	0.0701	424	413
Toluene	0.281	0.234	0.0658	422	409
<i>m</i> -Xylene	0.282	0.243	0.0634	420.5	408
<i>o</i> -Xylene	0.288	0.228	0.0657	422.5	410
<i>p</i> -Xylene	0.279	0.225	0.0628	419.5	407.5
Mesitylene	0.267	0.227	0.0606	417.5	406
Fluorobenzene	0.361	0.218	0.0787	—	—
Chlorobenzene	0.338	0.235	0.0794	436.5	422
Bromobenzene	0.340	0.244	0.0830	440.5	426

TABLE I  
 (Continued)

Solvent	$W$	$f(n^2)$	$W \cdot f(n^2)$	$\lambda_I$	$\lambda_{II}$
Iodobenzene	0.354	0.260	0.0920	443	434
<i>o</i> -Dichlorobenzene	0.363	0.242	0.0878	443	429.5
<i>m</i> -Dichlorobenzene	0.311	0.241	0.0750	—	—
1-Bromonaphthalene	0.366	0.269	0.0985	455	441.5
Carbon disulphide	0.264	0.260	0.0686	424.5	417.5
Dimethyl sulphoxide	0.470	0.220	0.1034	455.5	442
Sulpholane	0.444	0.222	0.0986	—	—
Triethyl phosphate	0.442	0.198	0.0875	—	—
Hexamethylphosphorous triamide	0.447	0.214	0.0957	447	434
Diethyl ether	0.331	0.178	0.0589	412.5	399.5
Dipropyl ether	0.330	0.187	0.0617	416	404
Diisopropyl ether	0.336	0.183	0.0615	415	404
Dibutyl ether	0.275	0.194	0.0534	—	—
Dioxane	0.352	0.202	0.0711	423.5	410
Tetrahydrofuran	0.387	0.197	0.0762	429	416
Tetrahydropyran	0.367	0.202	0.0741	—	—
1,2-Dimethoxyethane	0.403	0.188	0.0758	428	415
Acetaldehyde	0.512	0.170	0.0875	438	422.5
Acetone	0.471	0.180	0.0848	433.5	421
2-Butanone	0.444	0.188	0.0835	433.5	420.5
3-Heptanone	0.401	0.198	0.0794	—	—
Cyclopentanone	0.426	0.207	0.0882	—	—
Cyclohexanone	0.410	0.213	0.0873	—	—
Isobutyl methyl ketone	0.406	0.194	0.0787	430	418.5
Acetylacetone	0.402	0.212	0.0852	438.5	422
Methyl formiate	0.475	0.175	0.0831	—	—
Ethyl formiate	0.417	0.182	0.0759	—	—
Methyl acetate	0.426	0.181	0.0771	—	—
Ethyl acetate	0.395	0.185	0.0731	422	411
Propyl acetate	0.372	0.190	0.0707	422.5	409
Isopropyl acetate	0.370	0.187	0.0692	421.5	407
Butyl acetate	0.350	0.189	0.0662	420	407.5
Ethyl trichloroacetate	0.360	0.212	0.0763	—	—
Ethyl chloroacetate	0.417	0.203	0.0847	—	—
$\gamma$ -Butyrolactone	0.476	0.202	0.0961	—	—
Ethyl malonate	0.406	0.200	0.0812	—	—
Ethyl benzoate	0.362	0.229	0.0829	436	424.5
Anisole	0.345	0.232	0.0800	—	—
Acetophenone	0.396	0.237	0.0939	448.5	434
Phenylacetone	0.400	0.231	0.0924	—	—
Triethylamine	0.235	0.194	0.0456	401	400

TABLE I  
(Continued)

Solvent	$W$	$f(n^2)$	$W \cdot f(n^2)$	$\lambda_1$	$\lambda_{11}$
Tributylamine	0.209	0.205	0.0430	398.5	396
N,N-Dimethylformamide	0.468	0.208	0.0959	446	434
N,N-Dimethylacetamide	0.467	0.207	0.0967	—	—
N-Methylpyrrolidone	0.447	0.218	0.0974	—	—
Pyridine	0.403	0.230	0.0927	448	435
Acetanhydride	0.457	0.193	0.0882	441	425
Acetonitrile	0.514	0.174	0.0894	439	425
Propionitrile	0.468	0.184	0.0861	438	422.5
Butyronitrile	0.460	0.189	0.0869	—	—
Benzonitrile	0.403	0.236	0.0951	449	434.5
Phenylacetonitrile	0.407	0.234	0.0952	—	—
Nitromethane	0.500	0.188	0.0940	445	428.5
Nitroethane	0.456	0.192	0.0875	441.5	423
Nitrobenzene	0.409	0.242	0.0990	454.5	439.5
N,N-Dimethylaniline	0.346	0.244	0.0830	440	427

of 1-nitro-2-(4'-dimethylaminophenyl)ethene (*I*) are predominantly described by the product term and that sensitivity of these changes to the medium belongs among the highest encountered with the indicators studied so far<sup>11-13</sup>.

In accordance with the original model of the method of product term, the  $f(D, n^2)$  term characterizes the magnitude of deformation polarization of solvent in the course of excitation of the solute molecule, its  $f(D)$  component (which characterizes the overall — deformation and orientation — polarization of the solvent molecules adjacent to the solute molecule before the excitation) being considered a measure of arrangement and compactness of the cybotactic layer of the solute molecule. Let us suppose that the deformation polarization obeys the Kirkwood–Onsager  $f(n^2)$  function and that all deviations from Eq. (1) (for all solvents) are due to the overall, equilibrium polarization, which does not precisely obey the  $f(D)$  function. Let us, therefore, replace the  $f(D)$  function in Eq. (1) by the effective function  $W$  of the total polarizability of solvent which can be expressed explicitly from Eq. (1) in the form of Eq. (4).

$$W = ((\bar{\nu} - A)/f(n^2) - C)/B \quad (4)$$

Using Eq. (4) we calculated  $W$  for 96 solvents from the solvatochromism of the two nitrostyrenes and further nine indicators whose spectra were also measured in gas phase and for which an excellent correlation with Eq. (1) was found<sup>13</sup>. The arithmetic

means of the  $W$  values thus found for the individual indicators are given in Table I. In this scale of the effective Kikrwood–Onsager functions one value is chosen by the definition, *viz.* the  $W$  value for gaseous state  $W = f(D) = 0$ .

Thus the suggested procedure for evaluation of the medium effect offers two terms for evaluation of contribution of nonspecific interactions, out of which only one contains the empirical solvent characteristic  $W$ .

A comparison of the calculated  $W$  and  $f(D)$  functions shows that they are markedly different for some solvents and very close for others. Distinct differences between these quantities are found for aromatic solvents and dioxane, interesting are also the significantly higher  $W$  values for acetonitrile, acetaldehyde, and nitromethane. We consider the interpretation of the higher  $W$  values of acetonitrile and nitromethane based on proton-donor character of these solvents to be inadequate, because *e.g.* in the case of the 1-nitro-2-(4'-dimethylaminophenyl)ethene studied, whose spectrum was also measured in alcohols<sup>9</sup> (*i.e.* in media of high proton-donocity), the solvatochromic effect of these alcohols satisfies quite well Eq. (2).

Very close are the  $f(D)$  and  $W$  values for dihalogenomethanes and carbon disulphide, which were recommended<sup>14</sup> for practical studies of the medium effect on infrared spectra. For this solvent set (pentane, hexane, cyclohexane, tetrachloromethane, tetrachloroethylene, trichloroethylene, carbon disulphide, dichloroethane, dichloromethane, dibromomethane, and diiodomethane), whose  $f(D)$  and  $f(n^2)$  functions are distinctly different and cover a broad scale, even the  $f(n^2)$  term of Eq. (1) was quite insignificant, and the correlation coefficient between the wavenumbers and the  $f(D, n^2)$  function was 0.997 for 1-nitro-2-(4'-dimethylaminophenyl)ethene.

In the previous papers<sup>11,14</sup> we suggested that, in evaluation of the medium effects, fast and slow processes must be differentiated (the rates above and below  $10^{12} \text{ s}^{-1}$ , respectively). The fast processes include *e.g.* the excitation of molecules to higher electronic and vibrational states, the slow ones include physical equilibria and some spectral properties which are not connected with the excitation process. For evaluation of the medium effect on the fast and the slow processes it is recommended to apply Eqs (5) and (6), respectively, as the relations for the studied property  $Y$ .

$$Y = A + B \cdot W \cdot f(n^2) + C \cdot f(n^2) \quad (5)$$

$$Y = A + B \cdot W + C \cdot W \cdot f(n^2) \quad (6)$$

The presence of the  $C \cdot W \cdot f(n^2)$  term in Eq. (6) is due to the fact that the states between which the equilibrium is studied (isomers, tautomers) undergo various fast motions whose extent is different in the two states, hence the equilibrium depends on the function of refractive index. Its product with  $W$  has the same meaning as that in the case of spectral excitation.

We carried out tests of applicability of the  $W$  parameters to evaluation of the medium effect on electronic spectra (10 systems), infrared spectra (10 systems), chemical and physical equilibria (10 systems), and reaction rates (10 systems). The results are given in Tables II–V which also present the regression coefficients  $B$  and  $C$ , absolute term  $A$  of Eqs (5) and (6), and the overall ( $R$ ) and partial ( $r$ ) correlation coefficients and standard deviations ( $\sigma$ ).

From Table II it is obvious that the application of the  $W$  function to evaluation of the medium effect on electronic spectra is satisfactory, and the role of the  $W \cdot f(n^2)$  term is dominant in the majority of cases. An exception is observed with the medium effect on the longest-wave absorption band of phenoxaz-3-one. This compound shows the lowest solvatochromism out of the compounds studied, the contributions of the two functions,  $W \cdot f(n^2)$  and  $f(n^2)$ , to the overall effect being comparable. Out of the ten systems considered, only the systems 1, 2, 6, and 10 were used for the calculation of the  $W$  characteristics.

Table III presents the evaluation of the medium effect on wavenumbers of stretching vibrations of ten different bonds by means of Eq. (5). The product term plays a dominant role in the correlation, as it was the case also with the electronic spectra.

TABLE II

Results of evaluation of medium effect on electronic spectra by means of Eq. (5),  $Y = \tilde{\nu}$

System	$n$	$A$	$-B$	$-C$	$R$	$\sigma$	$r^a$
1 <sup>b</sup>	60	27.96	51.19	3.69	0.996	0.096	0.992
2 <sup>c</sup>	60	28.47	44.51	5.25	0.994	0.104	0.984
3 <sup>d</sup>	46	24.87	11.52	5.98	0.936	0.824	0.824
4 <sup>e</sup>	31	30.01	46.66	3.04	0.994	0.094	0.993
5 <sup>f</sup>	30	58.36	117.7	16.38	0.987	0.410	0.979
6 <sup>g</sup>	27	26.90	36.46	6.78	0.999	0.059	0.984
7 <sup>h</sup>	21	32.88	28.16	7.42	0.982	0.089	0.973
8 <sup>i</sup>	25	32.91	32.93	8.68	0.995	0.068	0.973
9 <sup>j</sup>	25	27.88	32.09	6.16	0.993	0.078	0.981
10 <sup>k</sup>	25	30.38	47.51	5.69	0.998	0.092	0.987

<sup>a</sup> The correlation coefficient of the dependence between  $\tilde{\nu}$  and  $W \cdot f(n^2)$ ; <sup>b</sup> 1-nitro-2-(4'-dimethylaminophenyl)ethene; <sup>c</sup> 2-nitro-1-(4'-dimethylaminophenyl)-1-propene; <sup>d</sup> phenoxaz-3-one<sup>18</sup>; <sup>e</sup> N,N-diethyl-3-methyl-4-nitroaniline<sup>19</sup>; <sup>f</sup> 1,3-diethyl-5-(5-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*i,j*]quinolizin-9-yl)-1,3-neopentylene-2,4-pentadienylidene)-2-thiobarbituric acid<sup>20</sup>; <sup>g</sup> 4-nitroanisole<sup>19</sup>; <sup>h</sup> N,N-dimethyl-4-aminobenzophenone<sup>19</sup>; <sup>i</sup> 1-nitro-2-(4'-methoxyphenyl)ethene<sup>19</sup>; <sup>j</sup> 3-nitro-N,N-diethylaniline<sup>19</sup>; <sup>k</sup> 4-nitro-N,N-diethylaniline<sup>19</sup>.

The results of evaluation of the medium effect on chemical and physical equilibria by means of Eq. (6) are presented in Table IV. Again, Eq. (6) satisfies the evaluation of medium effect very well; however, comparison of the partial correlation coefficients shows that the overall solvent polarizability characterized by  $W$  plays the dominant role in some cases only (the systems 22, 23, 24, 28, 29, and 30), whereas in the rest the product function  $W \cdot f(n^2)$  also plays a significant role.

The results of evaluation of the medium effect on rate constants of ten reactions by means of Eq. (6) are given in Table V. The results obtained are very interesting: except for the reaction No 34 the dominant role in the evaluation of medium effect is played by the cross term  $W \cdot f(n^2)$ , the contribution of the  $W$  function itself being quite insignificant in the reactions Nos 31, 33, 38, 39, and 40. The reaction of tripropylamine with methyl iodide is significant for the medium effect problem. Jungers and Lassau<sup>15</sup> measured the rate constants of this reaction in a large number of solvents, and  $\log k$  of this reaction (at 293.15 K) is often denoted as empirical polarity scale  $\varphi$  (ref.<sup>2</sup>). We have measured the rate constant of this reaction at the same conditions as the authors<sup>15</sup> in three further solvents in which the rate constant was not determined and which we consider important for these studies: in dimethyl

TABLE III  
Results of evaluation of medium effect on valence vibrations by means of Eq. (5),  $Y = \tilde{\nu}$

System	$n$	$A$	$B$	$C$	$R$	$\sigma, \text{cm}^{-1}$	$r^a$
11 <sup>b</sup>	20	1 710	-209.3	-26.35	0.978	1.5	0.964
12 <sup>c</sup>	15	1 737	-202.5	-28.6	0.978	1.5	0.963
13 <sup>d</sup>	13	1 104	-463.0	-17.6	0.989	2.2	0.988
14 <sup>e</sup>	11	1 289	-301.3	-30.1	0.990	1.6	0.980
15 <sup>f</sup>	11	3 682	-631.0	-53.5	0.974	5.3	0.969
16 <sup>g</sup>	11	3 658	-739.4	-58.0	0.926	11	0.921
17 <sup>h</sup>	10	3 500	-550.5	22.5	0.937	5.8	0.935
18 <sup>i</sup>	9	1 715	-250.8	-19.1	0.972	1.5	0.968
19 <sup>j</sup>	10	1 664	-365.4	7.2	0.990	1.6	0.989
20 <sup>k</sup>	13	1 760	-264.2	-17.9	0.988	0.9	0.987

<sup>a</sup> The correlation coefficient of the dependence between  $\tilde{\nu}$  and  $W \cdot f(n^2)$ ; <sup>b</sup> valence vibration of C=O bond in acetophenone<sup>21</sup>; <sup>c</sup> valence vibration of C=O bond in acetone<sup>21</sup>; <sup>d</sup> valence vibration of S—O bond in dimethyl sulphoxide<sup>21</sup>; <sup>e</sup> valence vibration of P—O bond in phosphorus oxychloride<sup>21</sup>; <sup>f</sup> valence vibration of O—H bond in methanol<sup>7</sup>; <sup>g</sup> valence vibration of O—H bond in phenol<sup>7</sup>; <sup>h</sup> antisymmetrical valence vibration of NH<sub>2</sub> group in aniline<sup>7</sup>; <sup>i</sup> valence vibration of C=O bond in chlorophyll *a*<sup>22</sup>; <sup>j</sup> valence vibration of *trans* N—O bond in isopropyl nitrite<sup>21</sup>; <sup>k</sup> valence vibration of C=O bond in *Z* conformer of methyl 2-fluorobenzoate<sup>25</sup>.



sulphoxide ( $\log k = 0.526$ ), dibromomethane ( $\log k = -0.26$ ), and diiodomethane ( $\log k = 0.72$ ).

Qualitative discussions of the medium effect on the quaternizations of amines with alkyl iodides usually start from the Eyring equation in thermodynamic interpretation:  $k = K^\ddagger kT/h$ , where  $k$  and  $h$  are the Boltzmann and the Planck constants, resp.,  $T$  stands for temperature, and  $K^\ddagger$  is the equilibrium constant between the activated complex and the reactants. Hence, the more polar is the activated complex as compared with the reactants, the more shifted is the equilibrium toward its formation by polar media and the faster the reaction. If, however, the reaction rate were affected by the medium in this way, it should depend mainly on the function  $W$  or  $f(D)$ . Similarly, if the hypothesis of the so-called active participation of solvent molecules in these reactions (*e.g.* ref.<sup>16</sup>) were justified, the reaction rate should depend on the dipole moments of the molecules of medium. However, the original Eyring theory also offers an interpretation of the observed dependence of  $\log k$  on the product function. Transformation of the activated complex into products is due to transformation of vibrational motion of one bond in the activated complex along the

TABLE IV  
Results of evaluation of medium effect on chemical and physical equilibria by means of Eq. (6)

System	$n$	$A$	$B$	$C$	$R$	$\sigma$	$r_w^a$	$r^a$
21 <sup>b</sup>	18	-18.54	14.87	110.7	0.980	0.40	0.856	0.918
22 <sup>c</sup>	23	21.78	-13.08	-154.1	0.991	0.52	0.981	0.931
23 <sup>d</sup>	32	0.93	5.87	3.89	0.952	0.20	0.951	0.884
24 <sup>e</sup>	12	2.47	-5.56	-0.47	0.983	0.13	0.983	0.945
25 <sup>f</sup>	7	-0.31	-0.58	18.72	0.962	0.09	0.919	0.960
26 <sup>g</sup>	13	1.94	-1.55	-9.43	0.951	0.11	0.927	0.938
27 <sup>h</sup>	13	1.80	-1.48	-10.44	0.953	0.11	0.928	0.937
28 <sup>i</sup>	11	-1.42	5.16	2.43	0.979	0.12	0.978	0.917
29 <sup>j</sup>	11	-3.11	5.95	-8.50	0.941	0.16	0.931	0.785
30 <sup>k</sup>	11	5.78	-8.98	-8.00	0.960	0.30	0.959	0.913

<sup>a</sup> Correlation coefficient  $r_w$  for the dependence between  $Y$  and  $W$ ,  $r$  for the dependence between  $Y$  and  $W \cdot f(n^2)$ ; <sup>b</sup> solubility of tetraethylammonium iodide in aprotic solvents<sup>23</sup>; <sup>c</sup> the Gibbs energy of the transition between methanol and other medium<sup>23</sup>; <sup>d</sup> solubility of nitromethane in aprotic solvents<sup>24</sup>; <sup>e</sup> the Gibbs energy of the transition between  $E$  and  $Z$  forms of methyl 2-fluorobenzoate<sup>25</sup>; <sup>f</sup> equilibrium between isomers of 1,2-dibromo-4-tert-butylcyclohexane<sup>26</sup>; <sup>g</sup> difference in the Gibbs energies of isomers of 2-isopropyl-5-methoxy-1,3-dioxane<sup>27</sup>; <sup>h</sup> difference in the Gibbs energies of 2-isopropyl-5-ethoxy-1,3-dioxane isomers<sup>27</sup>; <sup>i</sup> keto-enol equilibrium in tert-butyl 2-picolyl ketone<sup>28</sup>; <sup>j</sup> keto-enol equilibrium in tert-butyl quinaldyl ketone<sup>28</sup>; <sup>k</sup> keto-enol equilibrium in acetylacetone<sup>29</sup>.

reaction coordinate into translational motion of the products. The medium in which the activated complex is present is in thermal equilibrium (the extent of polarization of the solvent is characterized by  $W$ ), but the demands of the vibrational motions of bonds, inclusive of the decomposition vibration along the reaction coordinate, depend on the product function  $W \cdot f(n^2)$ , as it is the case with infrared spectra, too. The higher the value of this function, the lower the energy demands of the critical vibration leading to the decomposition of the activated complex, and the faster the reaction. This interpretation stands in accordance with the finding<sup>2</sup> that the activation entropy of these reactions increases in media with higher  $W \cdot f(n^2)$  function. The distinct role of deformation polarization of solvent within the overall solvent effect prompts us to be careful in current determinations of dipole moment of the activated complex from the dependence of  $\log k$  on the functions of relative permittivity alone.

As for relations of the  $W$  characteristics suggested to other solvent characteristics, we carried out correlations of  $W$  with the  $E_T(30)^N$  parameters by Reichardt<sup>2</sup>, the  $\pi^* + \delta\delta$  parameters by Kamlet and Taft<sup>1</sup>, and the AP, BP, EP, PP parameters by Pytela<sup>3</sup>. The following correlation equations were obtained:

TABLE V  
Results of evaluation of medium effect on reaction rates by means of Eq. 6

System	$n$	$A$	$B$	$C$	$R$	$\sigma$	$r_W^a$	$r^a$
31 <sup>b</sup>	15	-4.01	-0.66	36.3	0.988	0.10	0.923	0.987
32 <sup>c</sup>	10	-8.12	6.51	61.8	0.991	0.16	0.890	0.969
33 <sup>d</sup>	11	-0.36	0.67	5.83	0.996	0.02	0.950	0.979
34 <sup>e</sup>	7	15.55	-14.8	-36.2	0.979	0.05	0.966	0.912
35 <sup>f</sup>	17	-8.81	43.6	49.8	0.969	0.19	0.835	0.946
36 <sup>g</sup>	19	-6.50	3.1	49.4	0.975	0.20	0.863	0.963
37 <sup>h</sup>	19	-5.61	3.0	47.0	0.974	0.20	0.861	0.962
38 <sup>i</sup>	22	-6.07	0.3	57.7	0.974	0.21	0.651	0.974
39 <sup>j</sup>	22	-5.38	0.2	51.4	0.980	0.17	0.685	0.980
40 <sup>k</sup>	50	-7.03	0.8	68.6	0.982	0.22	0.842	0.981

<sup>a</sup> Correlation coefficient  $r_W$  for the dependence between  $Y$  and  $W$ ,  $r$  for the dependence between  $Y$  and  $W \cdot f(n^2)$ ; <sup>b</sup> thermal decomposition of tert-butyl performate<sup>30</sup>; <sup>c</sup> solvolysis of *p*-methoxyneopentyl tosylate<sup>31</sup>; <sup>d</sup> autooxidation of styrene<sup>32</sup>; <sup>e</sup> thermolysis of  $\alpha$ -chlorobenzylmethyl ether<sup>33</sup>; <sup>f</sup> reaction of 1,4-diazabicyclo[2,2,2]octane with (2-chloroethyl)benzene<sup>34</sup>; <sup>g</sup> reaction of 1,4-diazabicyclo[2,2,2]octane with (2-bromoethyl)benzene<sup>34</sup>; <sup>h</sup> reaction of 1,4-diazabicyclo[2,2,2]octane with (2-iodoethyl)benzene<sup>34</sup>; <sup>i</sup> reaction of triethylamine with ethyl bromoacetate<sup>35</sup>; <sup>j</sup> reaction of triethylamine with ethyl iodoacetate<sup>35</sup>; <sup>k</sup> reaction of tripropylamine with methyl iodide<sup>15</sup>.

$$E_{T(30)}^N = -0.018 + 1.836W \cdot f(D) - 0.051W \cdot f(n^2) \quad (7)$$

$$R = 0.963, \sigma = 0.03, r_{E_{T(30)}^N - W \cdot f(D)} = 0.963, n = 65$$

$$\pi^* = -0.95 + 14.86W \cdot f(n^2) + 2.01f(n^2) \quad (8)$$

$$R = 0.985, \sigma = 0.06, r_{\pi^* - W \cdot f(n^2)} = 0.975, n = 65$$

$$W = 0.22 + 0.287(\pi^* - 0.30\delta) \quad (9)$$

$$R = 0.947, \sigma = 0.05, n = 36$$

$$W = 0.40 + 0.044 AP + 0.012 BP + 0.303 EP + 0.119 PP \quad (10)$$

$$R = 0.974, \sigma = 0.02, n = 39.$$

Equation (8) expresses an excellent interpretation of the  $\pi^*$  parameters by Kamlet and Taft and a very real assessment of  $\pi^*$  of the gaseous state  $\pi_g^* = -0.95$  (ref.<sup>17</sup>).

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*Note added in proof:* Significant'y better than mentioned product of the Onsager's functions of relative permittivity ( $D$ ) and refractive index ( $n$ ) suits for the correlation of solvent shifts in electronic spectra the product of the Born's functions of relative permittivity and refractive index in the form:  $\Delta\tilde{\nu} = k \cdot (D - 1)/D \cdot (n^2 - 1)/n^2$ .