

TABLE II
 Franck-Condon factors and r -centroids of $B^3\Pi_1 - X^1\Sigma$ system of InCl molecule

v'	v''	0	1	2	3	4	5
0	<i>a</i>	0.586	0.291	0.092	0.024	0.006	0.001
	<i>b</i>	2.368	2.314	2.267	2.226	2.190	2.157
	<i>c</i>	3498.9	3538.0	3577.5	36.187		
1	<i>a</i>	0.333	0.128	0.284	0.165	0.063	0.019
	<i>b</i>	2.435	2.372	2.318	2.271	2.230	2.193
	<i>c</i>	3459.2		3535.3	3574.6	3614.5	3654.9
2	<i>a</i>	0.072	0.391	0.004	0.183	0.190	0.101
	<i>b</i>	2.516	2.349	2.375	2.321	2.275	2.234
	<i>c</i>	3419.6	3453.8		3532.8	3571.8	3611.4
3	<i>a</i>	0.008	0.162	0.323	0.023	0.088	0.172
	<i>b</i>	2.617	2.580	2.443	2.379	2.325	2.279
	<i>c</i>	3381.9	3418.3				3569.3
4	<i>a</i>	0.000	0.025	0.240	0.216	0.082	0.022
	<i>b</i>	2.752	2.621	2.524	2.447	2.383	2.329
	<i>c</i>		3381.1	3417.1			

a—Franck-Condon factors; *b*— r -centroids; *c*—Wavelengths in A.U.

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RELAXATION TIMES AND ACTIVATION ENERGIES OF SUBSTITUTED TOLUENES AND THEIR DIPOLAR MIXTURE

THE present communication reports the relaxation times and activation energies of 3-fluoro-6-amino toluene, 3-fluoro-6-nitro toluene and their dipolar mixtures in dilute solutions of benzene at 3 cm microwave

region. The measurements have been made at 20°, 30° and 40°C, in order to calculate free energies of activation for the process of dipole orientation and viscous flow. It has been concluded that the molecules are relaxed predominantly by a process of overall molecular rotation, and relaxation time of dipolar mixture is the average of the relaxation times of the two molecules.

Relaxation times τ were determined from the fixed frequency method of Gopala Krishna¹ for dilute solutions as discussed in an earlier paper². Standing wave technique of Roberts and Von Hippel³ was used for measurement of dielectric constant ϵ' and the loss factor ϵ'' . Activation energies have been calculated using Eyring's⁴ equation.

All the substances used are of L.R. grade (B.D.H.). Analar benzene (B.D.H.) has been distilled before use. The values of relaxation time and thermodynamic parameters are reported in Table I.

It is observed from the table that the relaxation time of 3-fluoro-6-amino toluene is smaller than that of 3-fluoro-6-nitro toluene. This is not only due to the smaller size of the former molecule but also due to the intramolecular rotation of the amino group round its bond with the ring.

It is evident from the table that the relaxation time obtained for dipolar mixture in benzene is the average of the two individual relaxation times of the polar components. The experimental results suggest that there is no association or complex formation, as

TABLE I
Values of relaxation times τ and thermodynamic parameters

Compounds	Temperature °K	$\tau \times 10^{12}$ sec	F_τ Kcal/mol	F_η Kcal/mol	S_τ Cal/mol	S_η Cal/mol	H_τ Cal/mol	H_η Kcal/mol
(i) 3-fluoro 6-amino toluene	293	8.02	2.26	2.90	-1.49	-1.29	1.82	2.52
	303	7.11	2.28	2.92	-1.51	-1.32	1.82	2.52
	313	6.07	2.31	2.94	-1.57	-1.34	1.82	2.52
(ii) 3-fluoro 6-nitro toluene	293	16.67	2.68	2.90	-0.92	-1.29	2.41	2.52
	303	15.12	2.74	2.92	-1.09	-1.32	2.41	2.52
	313	13.98	2.80	2.94	-1.21	-1.34	2.41	2.52
(iii) 3-fluoro-6-nitro toluene + 3-fluoro-6-amino toluene	293	12.83	2.53	2.90	-1.02	-1.29	2.23	2.52
	303	11.47	2.57	2.92	-1.12	-1.32	2.23	2.52
	313	10.29	2.61	2.94	-1.21	-1.34	2.23	2.52

where τ = Relaxation time;
 F_τ = Activation energy for dipole orientation;
 S_τ = Entropy of activation for dipole orientation;
 H_τ = H.at of activation for dipole orientation;
 F_η = Activation energy for viscous flow;
 S_η = Entropy of activation for viscous flow;
 H_η = Heat of activation for viscous flow.

otherwise the relaxation times would be different. A similar result has been obtained earlier by one of the authors⁵. This conclusion is in conformity with the fact that in dilute solutions, the dipole-dipole interaction is considerably reduced.

The free energies of activation, for the process of dielectric relaxation and the viscous flow increase with temperature and size of the molecules. Similar results have earlier been obtained by Smyth and collaborators⁶⁻⁸ and also by the present authors⁹. This is possible because at higher temperatures the molecular collision rate increases. The entropies of activation are found to be negative indicating that the activated state is more ordered than the normal state. Further, the heats of activation and energies of activation for viscous flow are greater than those for dipole relaxation, since the former involves both rotation and translation, while the latter only rotation.

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