Table 3. Second-order rate constants and energies and entropies of activation of the three organic phosphorus compounds.

Compound	k_2^{15} l mole ⁻¹ sec ⁻¹	k_2^{25} l mole ⁻¹ sec ⁻¹	k_2^{35} l mole ⁻¹ sec ⁻¹	E_a kcal. mole ⁻¹	$\Delta S^\ddagger$ E.U.
Dimethylamido-methyl-phosphoryl fluoride	—	1.04 ± 0.04	1.99 ± 0.02	11.9 ± 0.9	-21 ± 3
Ethylthio-methyl-phosphoryl fluoride	$(1.36 \pm 0.06) \times 10^4$	$(1.95 \pm 0.05) \times 10^4$	—	6.2 ± 1.2	-22 ± 4
Dimethylamido-ethoxy-phosphoryl cyanide	—	7.49 ± 0.08	13.0 ± 0.18	10.1 ± 0.4	-23 ± 1

$(0.40 \pm 0.02) \times 10^{-4}$ sec⁻¹ at 25°C and $(0.44 \pm 0.11) \times 10^{-4}$ sec⁻¹ at 35°C. The values of k_2 and the energies and entropies of activation for the alkaline hydrolysis of Tabun are given in Table 3.

Experimental. The syntheses of the two Sarin analogues have recently been published⁸ and Tabun was synthesized according to Holmstedt⁹. In the kinetic experiments performed with the automatic titrator³ the concentrations of the dimethylamino derivative and of Tabun were 0.40 mM and of the ethylthio derivative 0.20 mM. The first one was titrated with 0.1 M sodium hydroxide and the latter two with 0.05 M sodium hydroxide. In other respects the procedure closely adhered to that described for the determination of the alkaline hydrolysis of Sarin¹. In the paper chromatography ascending technique was used and 50 μ l in portions of 5 μ l of a 1 % aqueous solution of the ethylthio derivative were placed on a filter paper (Whatman No. 1). *Solvent:* Tert.-butanol: isopropanol: 2 M ammonium hydroxide (2:2:1). *Reagents:* Ammonium molybdate + hydrogen sulphide for the development of phosphorus¹⁰ and N-ethyl-maleinimide for sulphur¹¹.

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The Influence of Anharmonicity upon the Vibrational Probability Densities and Mean Amplitudes in Molecules. The General Case of a Polyatomic Molecule with Non-Degenerate Normal Vibrations

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The vibrational probability density for a general polyatomic molecule with non-degenerate normal vibrations and without accidental degeneracies has been calculated to terms of second order, making use of the Hamiltonian introduced by Darling and

Dennison¹, Herzberg², and Wilson, Decius and Cross³. The eigenvalues and eigenfunctions have been calculated by a standard second order perturbation calculation, and the summations over the different states have been performed by methods similar to those employed in the authors papers^{4,5}, the resulting probability density being

$$w(q_1, q_2, \dots, q_f) = w^0 (1 + a_0 + \sum_r a_r q_r + \sum_{r \leq s} \sum_s a_{rs} q_r q_s + \sum_{r \leq s} \sum_{s \leq t} \sum_t a_{rst} q_r q_s q_t + \sum_{r \leq s} \sum_{s \leq t} \sum_{t \leq u} \sum_u a_{rstu} q_r q_s q_t q_u + \sum_{r \leq s} \sum_{s \leq t} \sum_{t \leq u} \sum_{u \leq v} \sum_v a_{rstuv} q_r q_s q_t q_u q_v) \prod_x \sum_x a_{rstuvx} q_r q_s q_t q_u q_v q_x$$

where

$$w^0(q_1, q_2, \dots, q_f) = \pi^{-f/2} \prod_{k=1}^f$$

$[\tanh(hc\omega_k/2kT)]^{1/2} \exp[-\tanh(hc\omega_k/2kT)q_k^2]$
We have here introduced the convenient dimensionless coordinates

$$q_k = 2\pi(c\omega_k/h)^{1/2} Q_k$$

where ω_k is the wave-number corresponding to the normal coordinate Q_k , c is the velocity of light, and h is Planck's constant. The first order coefficients a_r and a_{rs} , as well as the second order coefficients a_0 , a_{rs} , a_{rstu} , and a_{rstuvx} have been calculated in terms of the potential constants of the Hamiltonian, the wavenumbers ω_k , and the absolute temperature T , the obtained results being somewhat complex.

The results have been applied to the cases of non-linear and linear symmetrical XY_2 molecules (in the latter case the degeneracy of one of the normal vibrations has to be taken appropriately into account), and numerical calculations have been performed for the molecules H_2O and CO_2 . The force constants have been obtained from Darling and Dennison¹ and Dennison⁶. The mean amplitudes

$$u_e^{AB} = [(R_{AB} - R_{AB}^{(e)})^2]^{1/2}$$

$$u_a^{AB} = [(R_{AB} - \bar{R}_{AB})^2]^{1/2}$$

$$u_m^{AB} = [(R_{AB} - R_{AB,m})^2]^{1/2}$$

as well as the mean values $\bar{R}_{AB}$ and the most probable values $R_{AB,m}$ of the deviations $r_{AB} = R_{AB} - R_{AB}^{(e)}$, have been calculated. R_{AB} is here the distance between the nuclei A and B, $R_{AB}^{(e)}$, $\bar{R}_{AB}$, and $R_{AB,m}$ are the equilibrium value, the

mean value, and the most probable value of R_{AB} , respectively. The results are listed in Tables 1 and 2.

Table 1. Mean amplitudes etc. for H_2O in Å units at $T = 300^\circ K$.

O—H	Harmonic	Anharmonic	H—H	Harmonic	Anharmonic
r_{OH}	0	0.0175	r_{HH}	0	0.0277
$r_{OH,m}$	0	0.0121	$r_{HH,m}$	0	0.0274
u_e^{OH}	0.0655	0.0707	u_e^{HH}	0.1088	0.1166
u_a^{OH}	0.0655	0.0687	u_a^{HH}	0.1088	0.1135
u_m^{OH}	0.0655	0.0689	u_m^{HH}	0.1088	0.1135

Table 2. Mean amplitudes etc. for CO_2 in Å units at $T = 300^\circ K$.

C—O	Harmonic	Anharmonic	O—O	Harmonic	Anharmonic
r_{CO}	0	0.0045	r_{OO}	0	0.0041
$r_{CO,m}$	0	0.0033	$r_{OO,m}$	0	0.0035
u_e^{CO}	0.0346	0.0351	u_e^{OO}	0.0395	0.0399
u_a^{CO}	0.0346	0.0348	u_a^{OO}	0.0395	0.0396
u_m^{CO}	0.0346	0.0349	u_m^{OO}	0.0395	0.0397

By electron diffraction Karle and Karle⁷ have obtained

$$u^{CO} = (0.034 \pm 0.003) \text{ Å}$$

$$u^{OO} = (0.040 \pm 0.007) \text{ Å}$$

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