DETERMINATION OF THE INTENSITY OF POLYCHROMATIC RADIATION IN THE REACTION COMPARTMENT AS A FUNCTION OF WAVENUMBER

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A procedure is suggested for studying the kinetics of photochemical reactions using excitation with polychromatic radiation, where the wavenumber dependence of the intensity of the polychromatic radiation entering the reaction compartment must be known. The observed relative intensities of the polychromatic source are calibrated by ferrioxalate actinometry, selected parts of the emission spectrum being eliminated by insertion of filters. The relative intensities of an HBO 200 high-pressure mercury lamp were measured. For the sake of brevity, the experimental data were fitted by a mathematical model (a polynomial), and only the parameters of the polynomial are presented in a tabular form.

Conventional monochromatic sources have a relatively low intensity, insufficient for quantitative examination of photochemical reactions exhibiting low quantum yields. Polychromatic sources, with higher radiation intensities, can be employed for this purpose provided that the intensities are known as a function of wavenumber[1]; hence, the sources must be intensity-calibrated over the entire spectral region used. Published actinometric methods[2-4] are based on the use of monochromatic radiation sources, or else they provide information on the total intensity of the source across a given spectral region.

In the present paper, a method is suggested for determining the wavenumber dependence of the number of photons entering the reaction compartment. The absolute intensity of radiation entering this compartment is calculated by multiplying the relative intensity by a constant specific for the particular experimental arrangement.

THEORETICAL

Photochemical Reaction Kinetics during Excitation with Polychromatic Radiation

The rate of photochemical conversion of substance A (the photochemically active substance) is given[5] by the product of the quantum yield of the reaction and the intensity of radiation absorbed by substance A (local rate); provided that only substance A is present in the solution and the latter is perfectly stirred, the local rate is identical with the mean rate, which for monochromatic radiation of wavenumber ν is

$$r_\nu = (S/V)\,\varphi I(1 - 10^{-\varepsilon l c_A})\,, \tag{1}$$

where φ is the reaction quantum yield at wavenumber ν, I is the intensity of radiation of wavenumber ν entering the reaction compartment, l is optical pathlength, ε is absorptivity of substance A at wavenumber ν, c_A is concentration of substance A in time t, S is irradiated area and V is the reaction compartment volume.

If polychromatic radiation is employed, the overall rate over the spectral region used is the integral sum of the partial rates,

$$r = 1/(\nu_m - \nu_n) \int_{\nu_n}^{\nu_m} r_\nu \, d\nu\,, \tag{2}$$

where ν_m and ν_n are the limiting wavenumbers of the polychromatic beam emitted by the source. Eq. (2) holds true only if substance A is present in a sufficient excess with respect to the product formed and if the absorption of radiation by the latter is negligible over the wavenumber region concerned.

Since integral (2) is analytically unsolvable, numerical integration will be performed, e.g. in the simplest form

$$r = (S/V)\,[1/(\nu_m - \nu_n)] \sum_{i=1}^{p} \varphi_i I_i (1 - 10^{-\varepsilon_i l c_A})\,\Delta\nu\,, \tag{3}$$

where $\Delta\nu$ is the integration step $(\nu_{i+1} - \nu_i)$,

$$\Delta\nu = (\nu_m - \nu_n)/p \tag{4}$$

and symbols with subscript i refer to wavenumber ν_i.

If the quantum yield[6] (φ_i) and absorptivity (ε_i) values of substance A are known, I_i can be calculated from Eq. (3) (source calibration). The aim of the procedure is to determine the intensities of radiation hitting the solution in dependence on wavenumber, $I_i = I(v_i)$. For this, the polychromatic radiation is passed through various absorption filters. The photochemical reaction rate in the actinometer for a given filter (labelled f) then is

$$r_f = (S/V)\,[1/(\nu_m - \nu_n)] \sum_{i=1}^{p} \varphi_i I_i T_{f,i} (1 - T_{A,i})\,\Delta\nu\,, \tag{5}$$

where $T_{f,i}$ is the transmittance of filter f at wavenumber ν_i and $T_{A,i}$ is the actinometer transmittance at this wavenumber.

The relative intensity J and the absolute intensity I are interrelated through

$$J_i = I_i/C\,, \tag{6}$$

where C is a constant, given by the experimental arrangement. The reaction rate then is

$$r_f = C(S/V)\left[1/(\nu_m - \nu_n)\right] \sum \varphi_i J_i T_{f,i}(1 - T_{A,i})\,\Delta\nu\,. \tag{7}$$

During photochemical conversion to a low degree, the right-hand side of this equation is a time-invariable constant. Thus, we can use the constants

$$K = C/(\nu_m - \nu_n) \tag{8}$$

and

$$S_f = \sum_{i=1}^{p} \varphi_i J_i T_{f,i}(1 - T_{A,i})\,\Delta\nu \tag{9}$$

and the reaction rate for a given filter then is

$$r_f = (S/V)\,KS_f\,. \tag{10}$$

Defining the reaction rate as the time increase in the amount of substance B (product) we have

$$(dc_B/dt)_f = (S/V)\,KS_f \tag{11}$$

the solution of which is

$$(c_B - c_B^0)_f/(t - t^0) = (S/V)\,KS_f\,, \tag{12}$$

where superscript ^{0} refers to the start of the reaction.

Mathematical Model of Emission Spectrum

The relative radiation intensity is defined by Eq. (*6*). Since the relative distribution of photons from discharge lamps was found not to vary appreciably with time, it was decided to model the emission spectrum of an HBO 200 (Narva) high-pressure mercury lamp by a suitable mathematical function. The emission spectrum of high-pressure mercury discharge lamps is a line spectrum to which an emission continuum is attached[5]. In conventional laboratory conditions, it begins with an emission maximum at 248 nm and ends with a maximum at 579 nm. The emission continues in the infrared region, where it is a continuum. The emission lines possess a width and a shape, given by interactions of the excited atoms[7]. Actually then, the spectrum is a band spectrum where the bands have a shape of sharp, asymmetric maxima. Optimization calculations revealed that the emission spectra can be well modelled by a Student statistical distribution function[8] in combination with a hyperbolic tangent (logistics). The entire emission spectrum thus is described by the polynomial

$$J_i = \sum_m K_m[1 + (1/P_m)(\nu_i - \mu_m)^2/\sigma_m]^{-(p_m+1)/2} + \\ + X_m/\{1 + C_m \exp[-X_m B_m(T_m - \nu_i)]\} , \qquad (13)$$

where K_m, P_m, σ_m, μ_m, X_m, C_m, B_m are parameters of the polynomial.

EXPERIMENTAL

The relative intensity distribution for the HBO 200 (Narva) high-pressure mercury lamp was measured over the 340–800 mn region by means of an OSA spectral analyzer (Spectronic, Munich) equipped with a Vidicon SIT 500 camera tube. The filter and actinometer transmittances were measured with a SPECORD UV-VIS recording spectrophotometer (Carl Zeiss, Jena).

Potassium ferrioxalate served as the actinometer; the quantum yield data for various wavenumbers were taken from the monographs[5,6] and values between them were obtained by three-point interpolation. The irradiated actinometer solution was treated conventionally[5,6].

Source Calibration

For the given experimental arrangement, the absolute total intensity of the radiation absorbed in the reaction space must be determined. A solution of the ferrioxalate actinometer is added to the reaction compartment (e.g., a cell). After closing, the stirred solution is irradiated with a beam of polychromatic radiation, which is passed through various absorption filters so that different parts of the emission psectrum are eliminated. After exposure, the concentration of ferric ions in the solution is quantitated, whereby the left-hand side of Eq. (*12*) is determined. The right-hand side of this equation is determined by measuring the transmittances of the actinometer solution and the absorption filter over the given spectral region. The S_f values are calculated by means of Eq. (*9*) using the polynomial (*13*). The constant K (Eq. (*12*)), and thus the constant C (Eq. (*8*)), is calculated by linear regression. The relative intensities are converted to absolute values according to Eq. (*6*).

RESULTS AND DISCUSSION

Eq. (*12*) is a straight line equation from which the unknown parameter K (defining the experimental arrangement) was calculated by linear regression. A series of absorption filters possessing different spectral characteristics was used. The independent variable values S_f were calculated by using Eq. (*9*). The dependent and independent variable values are given in Table I. The K value (in 10^{-17} mol s^{-1} cm^{-1}), standard deviation s_K (in the same units) and correlation coefficient r, as obtained from the experimental data (emission spectrum), are 101·7, 0·97 and 0·994, respectively; the values calculated from polynomial (*13*) (model of the emission spectrum) are 99·0, 0·79 and 0·995, respectively.

As mentioned above, it is inconvenient to store the relative photon distribution data of the lamp in the form of an extensive table of J_i, ν_i values. We approximated the data by the polynomial (*13*) and optimized it to obtain its parameters (Tables II and III). The accuracy of the fit was verified by numerical integration of

$$P = \sum J_i \, \Delta\nu \,, \qquad (14)$$

TABLE I

Values of the indepent variable S_f (Eq. (*9*)) and the dependent variable (Eq. (*12*)) for measurement sets 1—4

Filter	$S_f \, . \, 10^{-9}$, cm^{-1}		$10^8(C_B - C_B^0)/(t - t^0)$, mol s^{-1} cm^{-1}			
	exp.	model (*13*)	1	2	3	4
1	0·0553	0·0533	6·9	7·67	7·28	6·96
2	0·0601	0·06207	6·57	5·62	6·27	5·43
3	0·0740	0·0746	7·33	8·50	8·99	9·02
4	0·3014	0·3058	30·39	33·28	34·23	34·80
5	0·3617	0·3658	40·08	37·83	33·67	34·51
6	0·4583	0·4639	44·45	41·66	44·14	45·00
7	0·5813	0·5915	64·20	58·66	57·55	61·40
8	0·588	0·6000	54·87	56·73	59·03	58·14
9	0·7873	0·7940	74·37	79·65	77·11	78·43
10	0·8189	0·8281	82·03	79·00	83·64	81·55
11	0·5249	0·5311	52·16	57·24	58·40	56·52

TABLE II

Parameters of polynomial (*13*) and their standard deviations *s*

m	$K_m \, . \, 10^{-6}$	$s_K \, . \, 10^{-5}$	μ_m	s_μ	σ_m	s_σ	p_m	s_p
1	0·205	0·23	27 384	1·67	21·86	1·95	936·9	—
2	0·4112	0·14	27 251	3·12	149·86	21·00	0·50	0·273
3	0·554	0·22	24 592	1·40	47·63	1·67	896·75	—
4	0·3057	0·38	24 443	1·73	104·57	1 800·00	0·013	—
5	0·7388	0·72	22 953	4·40	39·87	3·40	989·20	—
6	0·7657	0·91	22 887	7·00	126·70	115·10	0·114	0·243
7	0·7955	1·6	18 341	0·95	6·25	1·08	995·50	—
8	2·601	0·57	18 271	1·28	67·58	1·97	2·68	0·93
9	2·653	0·49	17 295	1·42	96·59	2·64	3·16	1·05

where P is the area bounded by the emission curve. The fit was assessed by comparing the areas bounded by the experimental curve and by the polynomial (*13*) (Table IV). Parameter K in Eqs (*9*) and (*12*) can also be calculated to assess the accuracy of the fit; if the experimental J_i data are replaced by those obtained from the polynomial (*13*) (Table I), an only slightly different K value is obtained by the regression (99·0 vs 101·7 – see above).

Thus it can be concluded that the method suggested is well suited to the determina-

TABLE III

Parameters of polynomial (*13*)

m	$X_m \,.\, 10^{-5}$	$B_m \,.\, 10^7$	T_m	C_m
1	0·2865	1·53	27 106	9
2	0·2145	41·4	24 636	9
3	0·2110	115·0	23 004	9
4	0·4010	12·7	21 163	9
5	−0·2870	−3·87	20 173	9
6	0·8640	3·19	18 200	9
7	0·3560	7·71	17 490	9
8	2·3000	2·22	18 225	9
9	−2·3000	−0·960	18 077	9

TABLE IV

Comparison of areas bounded by the emission spectral curve, P, as obtained from experimental data and by the polynomial (*13*)

Emission maximum	Wavenumber, cm^{-1}		$P \,.\, 10^{-6}$		Difference %
	upper	lower	exp.	polynomial (*13*)	
1	27 992	25 318	245·98	243·06	+1·2
2	25 318	24 046	160·98	168·69	−4·6
3	24 046	21 374	477·25	484·18	−1·4
[a]	21 374	19 768	166·59	179·87	−7·4
4	19 768	17 649	848·00	779·00	+8·8
5	17 649	17 089	815·60	808·80	+0·8
1–5	27 992	17 089	2 714·4	2 663·6	+1·9

[a] Continuum between maxima 3, 4.

tion of the intensity of polychromatic radiation entering the reaction compartment, which facilitates the use of polychromatic radiation in photochemical kinetics studies.

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