Photochemistry of Complex Ions. III. Absolute Quantum Yields for the Photolysis of Some Aqueous Chromium(III) Complexes. Chemical Actinometry in the Long Wavelength Visible Region

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Abstract: Absolute quantum yields are reported for the photoaquation of aqueous Reinecke's salt, $KCr(NH_3)_2(NCS)_4$, and of $Cr(urea)_6Cl_3$ at 23° for a number of wavelengths between 316 and 750 mμ and between 452 and 735 mμ, respectively. Detailed procedures are given so that these systems may be used for chemical actinometry. The respective apparent activation energies are 1.3 and 3.0 kcal/mole. In addition, pH-dependence studies on the first system indicated that while only one thiocyanate is released per primary act, in alkaline solutions the remaining three are rapidly hydrolyzed off. Less complete data are reported for aqueous $K_3Cr(NCS)_6$. Again, only one thiocyanate is released in the primary act, but the remaining five are hydrolyzed off rapidly in alkaline solution. Some photoaquation quantum yields are also reported for aqueous $Cr(NH_3)_6(NO_3)_3$. The data include a number of quantum yield determinations in the region of the doublet absorption bands.

A number of investigations have been carried out in this laboratory on the photolytic behavior of transition metal complexes,[1] and one major emphasis has been on the wavelength dependence both of quantum yield and of mode of reaction. Other laboratories similarly have been interested in this subject.[2] These complexes generally are colored so that the wavelength region of interest typically extends from the quartz ultraviolet to the deep red; the same is true for those aspects of the current extensive interest in organic photochemistry where colored substances are involved.

Exploitation of this relatively recent surge of interest in the photochemistry of colored substances has been handicapped by the experimental difficulty of obtaining accurate quantum yields without becoming involved with the rather formidable procedures of absolute photometry. Alternatives have been to report relative quantum yields only, sometimes corrected by the quite unreliable manufacturer's estimates of the variation of lamp output with wavelength, or to use chemical actinometers. These last, where accurately calibrated, can be very convenient. In particular, the uranyl oxalate[3] and the ferric oxalate actinometers[4] have been very widely used. These are both reasonably easy to use and the latter, in particular, is quite sensitive. Both, however, have the limitation of being usable only in the ultraviolet and near-ultraviolet; absorption limits the range of the uranyl oxalate system to light of wavelength shorter than 450 mμ, and that of the ferric oxalate system to perhaps 500 mμ at the outside. In the past we have used the expedient of calibrating the geometry of a nonabsolute bolometric system by means of the ferric oxalate actinometer and then using the bolometer for measurements at longer wavelengths,[1] but the need for a good actinometric system whose absolute calibration extend to at least 700 mμ has been acute.

The only system having even approximately such qualifications has been that developed by Warburg and Schocken[5] which is based on the ethylchlorophyllic or protoporphyrine sensitized oxygen oxidation of thiourea. It is necessary to measure the reacted oxygen manometrically, and the procedure is neither simple nor highly sensitive; it is limited to the range 420 to 650 mμ. It has been with this situation in mind that we have felt it worthwhile to obtain the absolute photoaquation quantum yields for several Cr(III) complexes whose photolysis can be detected with great sensitivity, whose range of light absorption extends from the ultraviolet to the deep red, and whose quantum yields are virtually wavelength independent.

The two systems offered here as chemical actinometers are aqueous $KCr(NH_3)_2(NCS)_4$ (Reinecke's salt) and $Cr(urea)_6Cl_3$. We reported earlier some limited quantum yield data for the former,[1a] as well as a detailed study of its thermal aquation reactions.[6] The absorption spectrum and low-temperature luminescence behavior of the hexaurea complex have been described

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(1) (a) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958); (b) A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960); (c) A. W. Adamson, *J. Inorg. Nucl. Chem.*, **13**, 275 (1960); (d) S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962); (e) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963); (f) A. W. Adamson, "Spectrospecific Photolysis of Aqueous $Cr(en)_2(OH)_2^+$ Ion," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965; (g) A. W. Adamson and J. R. Perumareddi, *Inorg. Chem.*, **4**, 247 (1965); (h) S. Penkett and A. W. Adamson, *J. Am. Chem. Soc.*, 87, 2514 (1965).

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(3) (a) W. G. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930); (b) L. J. Heidt and F. Daniels, *ibid.*, **54**, 2384 (1932); (c) F. P. Brackett and G. S. Forbes, *ibid.*, **55**, 4459 (1933); (d) G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934); (e) J. N. Pitts, J. D. Margerum, R. P. Taylor, and W. Brim, *ibid.*, 77, 5499 (1955); (f) K. Porter and D. H. Volman, *ibid.*, 84, 2011 (1962).

(4) (a) C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956); (c) C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, **63**, 22 (1959); (d) J. Lee and H. H. Seliger, *J. Chem. Phys.*, 40, 519 (1964).

(5) O. Warburg and V. Schocken, *Arch. Biochem.*, **21**, 363 (1949); *Naturwiss.*, 42, 449 (1955).

(6) A. W. Adamson, *J. Am. Chem. Soc.*, **80**, 3183 (1958).

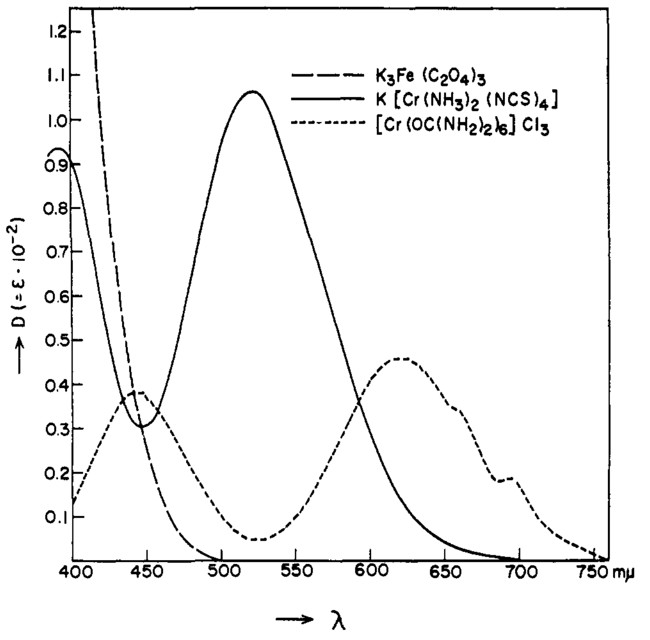

Figure 1. Absorption spectra for three actinometric systems.

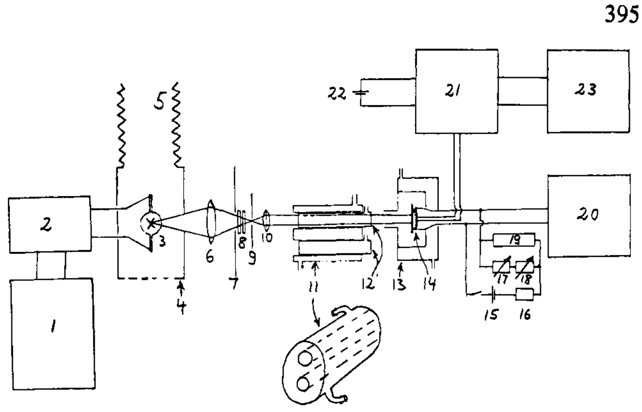

Figure 2. Block diagram of the equipment for quantum yield determinations.

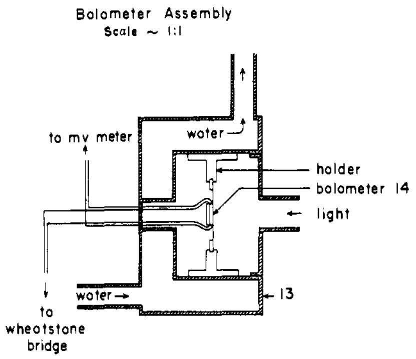

Figure 3. Bolometer detail.

by Porter and Schläfer[7] and the thermal aquation rate is likewise known.[8,9] Briefly, in both cases there is an efficient photoaquation of nearly wavelength independent quantum yield, relatively small thermal aquation correction, and detection methods for determining accurately less than 0.1% reaction. The spectra, along with that of the ferric oxalate complex for comparison, are shown in Figure 1, and it is seen that $KCr(NH_3)_2(NCS)_4$ may be used with ease out to 600 mμ and, with more difficulty, out to 735 mμ while $Cr(urea)_6Cl_3$ absorbs sufficiently for easy use out to 735 mμ.

Some additional results are reported, in connection with the third part of this paper, on photoaquation yields for $Cr(NCS)_6^{-3}$, and for $Cr(NH_3)_6^{+3}$, where a good quantum yield value has been obtained for light in the region of the doublet absorption band.

I. Quantum Yield Determinations

A. Experimental. (1) The Photochemical Equipment. A block diagram of the general setup is shown in Figure 2. A 900-w Hanovia compact arc xenon lamp (Catalog No. 538C-9) (3) was powered by a Chirstie SCR regulated dc power supply (Model BCX 600-1) (1), in conjunction with a Hanovia universal starter (Catalog No. 29011) (2). The lamp was positioned vertically in a 30-cm high by 12.5-cm diameter cylindrical brass housing (4) which was cooled by water flow through copper tubing wound on the outside. The housing was open at the bottom and the lamp was cooled, and ozone vented, by sucking air through a vent at the top of the housing into the general hood system of the laboratory.

The intense region of the arc is only about 1 mm long so that excellent collimation was obtained by means of glass lenses (7.5-cm focal length (6) and 5-cm focal length (10)), with the aperture controlled by two diaphragms (7 and 9), so that a final, virtually parallel beam of 1-cm diameter resulted. Monochromatization was by means of suitable interference and Corning glass blocking filters (8), with the former facing the beam so as to reduce heating in the filters. A shield could be swung in position between (8) and (9) to interrupt the light beam.

The collimated, monochromatized beam passed through a 10-cm Beckman spectrophotometer cell (12). Both it and a matching cell were held in a double-walled brass holder (11) through which water thermostated to ±0.02° was circulated; the matching cell contained solution identical with that being irradiated so that accurate correction for dark reaction and blank could be made.

The light beam then impinged on a bolometer, whose detail is shown in Figure 3. The sensitive element (14) consisted of a disk of aluminum foil, blackened with a thin uniform layer of benzene soot, and mounted on a stiff cardboard ring which in turn was held in place by a notched plexiglass ring (24). This slid snugly into a double-walled brass holder through which water thermostated to ±0.02° was pumped (13). Even with this heat isolation, it was further helpful to shield the housing and leads (13) from room drafts by a loose plastic covering (not shown). The temperature of the aluminum ring was measured by means of a 10^5-ohm Glennite Thermistor (Catalog No. 51TGl, Gulton Industries, Inc., Metuchen, N. J.) whose temperature coefficient was −5.4%/deg. It's resistance was determined by means of a Wheatstone bridge circuit (Cenco, Catalog No. 83295) (see Figure 2 (21)) and, a vacuum tube nullmeter (Honeywell microammeter

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(7) G. E. Porter and H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), **37**, 109 (1963).

(8) M. Kilpatrick, *J. Am. Chem. Soc.*, **50**, 358 (1928).

(9) K. B. Yatsimirskii and E. I. Yasinskene, *Zh. Obshch. Khim.*, **24**, 55 (1954).

Table I

Wave-length, mμ	Interference filter[a]	Corning glass filter[b]	Transmission at maximum, %	Half-width, mμ
350	BL 33-78-50	CS 7-60	34	23
358	BA	CS 7-60	19	18
392	BL 33-78-39	CS 0-52 + CS 4-97	41	12
416	BA	CS 4-97	45	10
452	BL 33-78-45	CS 3-73 + CS 4-97	33	7
504	BL 33-78-50	CS 3-72 + CS 4-96	38	10
520	BL 33-78-52	CS 3-72 + CS 4-96	41	10
545	BA	CS 3-70 + CS 4-96	80	6
585	BL 33-78-58	CS 3-70 + CS 1-69	40	9
600	BL 33-78-60	CS 3-66 + CS 1-69	38	10
628	BL 33-78-63	CS 3-66 + CS 1-69	38	10
652	BL 33-78-65	CS 2-62	32	9
676	BL 33-78-67	CS 2-59	38	8
696	BA	CS 2-59 + CS 1-69	70	9
713	BA	CS 2-64 + CS 1-69	74	8
735	BL 33-78-73	CS 2-64	41	12
750	BL 33-78-75	CS 2-64	42	14

[a] BL: Bausch and Lomb, Inc., Rochester 2, N. Y.; BA: Baird-Atomic, Inc., Cambridge 38, Mass. [b] Corning Glass Works, Corning, N. Y.

Model 104 WIG) (23), using a 1.5-v battery (22) as power source.

The bolometer was operated as a steady-state instrument. That is, it was allowed to come to equilibrium with the impinging light beam; because of its low heat capacity, this only required a few minutes. The bolometer also contained a fine grid of resistance wire (10-cm length, 10.4 ohm) pasted to the back of the aluminum foil with silicone rubber (General Electric RTV 102); the thermistor was actually on the back of the resistance grid, and a back cover of aluminum foil was cemented over the thermistor. From front to back, the sensor then consisted of soot, aluminum foil, silicone cement, resistance wire, silicone cement, thermistor, silicone cement, and aluminum foil. Its total thickness was about 3 mm.

The resistance grid was used to provide a known amount of electrical heating; it was connected to a high input resistance millivoltmeter (Beckman 101900 Research pH meter) (Figure 2 (20)), and a variable current source consisting of a 1.5-v battery (15) and fixed and variable potentiometer type resistances (17, 18, 19). The procedure was then to allow a steady-state temperature to be reached with the light beam incident on the bolometer, then to interrupt the beam, switch in the resistance heating circuit, and adjust the current flow so that the same steady-state temperature was provided. By working back and forth between light and resistance heating, a setting would finally be reached such that the steady-state temperature remained independent of heat source. The power input of the light beam was thus matched to the power input through resistance heating, with the latter given by $W = V^2/R$.

In general the power levels involved were about 10^{-3} w so that the voltage drop to produce equivalent heating by the resistance grid was about 100 mv. It should be noted that the power input was low enough that the actual heating of the sensor assembly was about 0.2°. No corrections for resistance changes with temperature were thus needed. The sensitivity of the bolometer was about 2×10^{-5} w so that measurements of light intensity were easily precise to 1%.

Several small corrections were considered in converting the watt power absorption, W, to einsteins per sec (*i.e.*, moles of light quanta per sec) in the beam. First, the albedo of soot is 0.05 to 0.03 for light of our region of wavelength,[10] and W was therefore multiplied by the factor 1.04. A small correction, 0.4%, was made to allow for the resistance of the lead wires from the resistance grid to the millivoltmeter. Reflection from the cell windows was determined by the reduction in intensity in the beam on interposing a water-filled cell, using green light, and redetermined from time to time. It varied from 3.6 to 4.0% per window, and the latter figure was used in making the correction, usually only needed for the front window since light absorption by the solutions being irradiated was generally greater than 99%.

Finally, the bolometer was found to be accurately linear in response up to at least 0.015 w. The procedure for determining this involved superimposing a variable electrical on a constant light heating and observing that the increment due to the light was invariant. The bolometer was sensitive enough that small room drafts could be noticed as a few thousandths of a degree fluctuation in steady-state temperature, but even this effect was largely eliminated by our procedure of matching light and electrical heating with alternating switching from one to the other as the final check on the equivalence of the two steady-state conditions. The xenon lamp output was stable over long periods to within 1%, the various corrections for absorbance of soot and reflection by windows should not be uncertain by more than about 1%, and the analytical procedures used were good to 1%. Over-all we estimate our absolute error to be ±3% and relative error to be ±1%.

(2) Monochromatization. As noted above, monochromatization was accomplished by means of selected interference and glass-blocking filters. The spectral characteristics of each were determined on a Cary Model 14 recording spectrophotometer to make certain that no secondary windows were left unblocked or that an undue amount of infrared light was being passed.

The characteristics of the various combinations are summarized in Table I.

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(10) F. Kohlrausch, "Praktische Physik," Vol. 1, B. G. Teubner Verlagsgesellschaft, Stuttgart, 1955, p 463.

(3) Quantum Yields for the Ferric Oxalate Actinometer. It was of interest to determine the extent to which our quantum yields and those of Hatchard and Parker[4] for the ferric oxalate system would agree. Their procedure was followed, using 6×10^{-3} *M* $K_3Fe(C_2O_4)_3$ irradiated in the 30-ml volume, 10-cm Beckman spectrophotometer cell previously described. Care was taken that the light beam never touched the side walls of the cell, to avoid the increase in quantum yields reported by Lee and Seliger.[4d] The solutions were not stirred as this was found to be unnecessary.

Table II. Photolysis Quantum Yields for 6×10^{-3} *M* $K_3Fe(C_2O_4)_3$ at 23°

Wavelength, mμ	Absorbed intensity, einstein/sec × 10⁹	% reaction/time, min	Quantum yield
358	0.351	1.52/10	1.26
		1.51	1.25
		1.50	1.25
392	1.12	2.35/5	1.13
		2.35	1.13
		2.37	1.14
416	1.21	2.35/5	1.13
		2.30	1.11
		2.32	1.12
	1.39	2.78	1.14
		2.68	1.10

Our results are given in Table II; each entry represents a complete, independent experiment, and the various determinations were distributed in time over the entire period of this investigation. The values at 392 and 416 mμ are in agreement with that of Parker and Hatchard[4c] (1.14 at 405 mμ). At 365 mμ they give a value of 1.16, based on uranyl oxalate calibration, and 1.26, based on the use of a calibrated thermophile; our values agree with the latter, and with the similar value found by Lee and Seliger.[4d]

(4) Materials and Analytical Procedures. Reinecke's salt is commercially available as the ammonium salt. This was converted to the potassium salt by dissolving in warm (40–50°) water, adding excess solid potassium nitrate, cooling, and filtering. The product was recrystallized from warm water containing a few per cent added potassium nitrate, washed with cold water, and dried over P_2O_5 in a vacuum desiccator to give the anhydrous product (which showed no loss in weight on heating at 110°). These operations should be carried out in dim red light if a minimum blank is desired in the later use of the salt. The product had virtually no free ammonia, as tested by Nessler's reagent.[11] It may be stored indefinitely if kept away from light. The ligand field bands are at 392 mμ (ε 93.5) and 520 mμ (ε 106.5).

The compound $Cr(urea)_6Cl_3$ was prepared according to the literature[12,13] in dim light. It was dried as above to give the anhydrous salt and can be stored if kept dry and dark. The ligand field bands showed absorption maxima at 444 mμ (ε 38.4) and 620 mμ (ε 46.9); this last figure is slightly different from that reported by Porter and Schläfer[7] (615 mμ and ε 52.8).

The compound $K_3Cr(NCS)_6$ was prepared by a standard procedure[13] and dried at 110° (it is also commercially available, Alfa Inorganics, Inc., Cr-115); similarly for the preparation of $Cr(NH_3)_6(NO_3)_3$ (*via* liquid ammonia medium[13]), which was recrystallized from water and dried in air and then over P_2O_5 in a vacuum desiccator.

The extent of either thermal or photochemical aquation of $KCr(NH_3)_2(NCS)_4$ was determined by analysis for free thiocyanate ion. An aliquot of the solution to be analyzed was accurately diluted (at least 4:1) into a reagent consisting of 0.1 *M* $Fe(NO_3)_3$ and 0.5 *M* $HClO_4$. The resulting iron thiocyanate complex has an absorption maximum at 450 mμ with an extinction coefficient of 4.30×10^3, and since the complex is unattacked, the optical density at this wavelength gives the thiocyanate ion concentration directly. In the case of $K_3Cr(NCS)_6$, it was found that the iron reagent catalyzed aquation, and the unreacted complex was therefore precipitated from the solution by means of excess $(CH_3)_4NCl$ before proceeding.

The procedure in the case of the hexaurea complex was less simple, as no easy and sensitive method for the detection of free urea is available. We therefore precipitated the unreacted complex as the perchlorate salt and determined chromium in the supernatant.[14] An aliquot of the solution to be analyzed was diluted to 25 ml to give a final concentration not higher than 0.015 *M*, and 3 ml of saturated aqueous sodium perchlorate was then added[15] to precipitate out the perchlorate salt. Chloride was then removed by adding 2 ml of 0.8 *M* silver nitrate solution, and the suspension was filtered. Ammonium peroxydisulfate (5 ml, 0.5 *M*) was then added to 5 ml of the clear (and colorless) filtrate, about 30 ml of distilled water, and a few drops of the silver nitrate solution. The solution was then boiled gently for 20 min over a low flame to complete the oxidation to Cr(VI) and to destroy the excess peroxydisulfate. The solution was then transferred to a 50-ml volumetric flask, water was added to bring the volume to about 40 ml, and then 3 ml of a solution of 0.3 g of 1,5-diphenylcarbohydrazide (Eastman Organic Chemicals) in 100 ml of absolute acetone (stable for about 1 week) was added, and the solution was made up to 50 ml with mixing. The chromium content was determined from the optical density at 546 mμ, using an extinction coefficient of 4.20×10^4; the measurement should be made within 40 min of the addition of the organic reagent. Essentially the same procedure was employed for determining the amount of photolyzed $Cr(NH_3)_6{}^{+3}$.

(5) Photolysis Procedures. The general procedure was as follows. Fresh solutions were made up for each run and, if more than 0.01 *M*, filtered. Their concentrations were chosen insofar as possible so that 99% or more of the incident light would be absorbed in the 10-cm cell. The light intensity was first determined

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(11) R. W. King and W. B. M. Faulconer, *Anal. Chem.*, **28**, 255 (1956).

(12) E. Wilke-Dörfurt and K. Niederer, *Z. Anorg. Allgem. Chem.*, **184**, 150 (1929).

(13) G. Brauer, "Handbuch der Präparativen anorganischen Chemie," Vol. 2, Ferdinand Enke Verlag, Stuttgart, 1962, p 1190.

(14) T. L. Allen, *Anal. Chem.*, 30, 447 (1958).

(15) The solubility of hexaureachromium(III) perchlorate in water is reported to be 0.006 *M* (A. Seidell, "Solubility of Inorganic and Metal Organic Compounds," Vol. 1, 3rd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p 443) so that under our conditions the amount remaining in the supernatant was negligible.

Table III. Quantum Yields for Photorelease of Thiocyanate by $KCr(NH_3)_2(NCS)_4$ at 23° and pH 5.3

Wavelength, mμ	Extinction coeff, ε	Concn, $M \times 10^3$	Absd intensity, einstein/sec $\times 10^9$	% photolysis/time, min	Quantum yield
316	11,000	1.1	1.41	3.56/20	0.294
				3.48	0.288
					Av. 0.291
350	>100	3.0	2.99	1.69/20	0.380
				1.71	0.392
				1.71	0.392
				1.69	0.388
					Av. 0.388
392 (absorption max)	93.5	5.0	11.6	3.33/20	0.323
				3.24	0.314
				3.26	0.316
				3.16	0.314
				3.16	0.314
					Av. 0.316
416	67.5	8.0	13.5	2.16/20	0.309
				2.14	0.306
				2.15	0.308[a]
				5.56/50	0.318
				5.83	0.310
					Av. 0.310
452 (absorption min)	31.2	10.0	6.76	0.93/20	0.309
				0.94	0.312
				0.95	0.315
				0.92	0.306
					Av. 0.311
504	97.5	5.0	12.4	3.31/20	0.300
				3.26	0.299
				3.26	0.299
				3.24	0.297
				3.26	0.299
					Av. 0.299
		22.5	127	3.37/10	0.288
		10.1		7.56	0.290
					Av. 0.289[b]
520 (absorption max)	106.5	4.0	14.7	3.51/15	0.287
				3.51	0.287
				4.71/20	0.288
				4.63	0.283
				4.68	0.286
					Av. 0.286
545	90.5	5.75	12.4	6.35/50	0.285
		5.63		6.44	0.282
		5.05	13.4	8.01	0.291
		5.00	11.1	6.50	0.281
				6.45	0.278
				6.55	0.283
				6.59	0.285
			11.2	6.46	0.275[a]
				6.64	0.282
		6.07		5.37	0.276
		5.00	11.7	6.78	0.279
		5.00	11.3	6.57	0.282[a]
			10.8	5.00/40	0.279
			11.4	5.39	0.285
			13.6	4.74/30	0.283
					Av. 0.282
585	43.8	10.0	13.2	1.58/20	0.269
				1.59	0.270
				1.58	0.269
				1.56	0.266
				1.61	0.274
					Av. 0.270
600	29.0	25.0	13.2	0.61/20	0.278
		24.7	13.4	0.62	0.275
		24.8		0.62	0.278
		25.2		1.50/50	0.272
					Av. 0.276

Table III (*Continued*)

Waveleagth, mμ	Extinction coeff, ε	Concn, $M \times 10^3$	Absd intensity, einstein/sec $\times 10^9$	% photolysis/time, min	Quantum yield
676	0.771	45.5	9.3	0.687/60	0.277
	0.708	43.2	8.9	0.665	0.265
	0.740	44.6	9.1	0.710	0.283
	0.722	46.4	9.4	0.656	0.265
	0.749	44.6	8.8	0.645	0.264
	Av. 0.748				Av. 0.271
713	0.348	46.2	4.56	0.434/80	0.282
	0.342	46.5	4.60	0.443	0.288
	0.349	45.6	4.52	0.491/90	0.283
	0.340	47.1	4.66	0.485	0.281
	Av. 0.35				Av. 0.284
735	0.296	44.2	6.08	0.651/80	0.306
	(0.395)	46.4	6.38	0.654	0.306
	0.259	44.8	6.33	0.652	0.294
	0.267	45.7	6.51	0.674	0.301
	Av. 0.27				Av. 0.302
750	0.162	49.4	6.31	1.14/178	0.259
	(0.247)	46.2	5.76	0.580/90	0.267
	0.156	48.1		0.650/100	0.280
	0.145	47.6	5.10	0.594	0.286
	Av. 0.15				0.273

[a] In 0.1 N H_2SO_4 medium. [b] Runs at high light intensity; see text.

with the cell filled with water (and redetermined at the end of the run). The two cells were then rinsed, dried, and filled with the solution to be photolyzed, and placed in the thermostated cell holder ((11), Figure 2) to come to thermal equilibrium; the lower cell remained in the dark and provided the control for correcting for blank and thermal aquation. The light beam was then allowed to pass through the upper cell, and the emergent intensity ascertained (it was ordinarily negligible) during the usually 20- to 30-min exposures. Separate experiments showed that some mixing was needed to eliminate secondary photolysis and/or inner filter effects in that it was found that unstirred solutions of $KCr(NH_3)_2(NCS)_4$ showed about 6% less photolysis than did stirred ones. In our case it was adequate to interrupt the light beam every 5 min and tilt the cell back and forth to allow a small air bubble (deliberately left in filling and which did not intercept the light beam) to cause mixing. At the end of the irradiation period, aliquots were taken from both the irradiated and the dark solutions and analyzed for degree of photoaquation by differential spectrophotometry.

Quantum yields were calculated as the moles of thiocyanate released per einstein of light absorbed (in the case of $KCr(NH_3)_2(NCS)_4$ and $K_3Cr(NCS)_6$) or as moles of original complex reacted per einstein of light absorbed (in the case of $Cr(urea)_6Cl_3$ and $Cr(NH_3)_6(NO_3)_3$).

(6) **Thermal Aquation Rates.** The thermal aquation kinetics of $Cr(NH_3)_2(NCS)_4^-$ has already been described in some detail[6] and for natural or acidic solutions the first-order rate constant for thiocyanate release was found to be 0.015 min^{-1} at 60°, with an activation energy of 27 kcal/mole. During the course of the current investigations we obtained additional data for 0.008 M solutions at pH 5.5–5.0 and 23°, which gave $k = 1.01 \times 10^{-4}$ min^{-1} or 0.6% of one thiocyanate per chromium per hour. This compares to the value 1.05×10^{-4} min^{-1} calculated from the earlier work.

While neither OH^- nor, from the previous work, CN^- affects the rate of the first step, it was found that in alkaline solution the remaining thiocyanates hydrolyze off rapidly (see below under pH dependence). From such studies we conclude that in neutral to moderately acid solutions, there is a relatively rapid equilibrium between $Cr(NH_3)_2(NCS)_3(H_2O)$ and $Cr(NH_3)_2(NCS)_2(H_2O)_2^+$ such that in the thermal aquation an average of 1.5 thiocyanates are released per parent complex reacted at 23°.

The same conclusion was reached *via* a different procedure. The optical density at 303 mμ (ϵ 1.52×10^4) provides a sensitive analysis for $Cr(NH_3)_2(NCS)_4^-$, and the concentration of unaquated complex was thusly determined for successive aliquots of a 0.008 M solution at 23° as thermal aquation occurred. It was necessary to correct for absorption due to partially aquated species, and this was done by precipitating the unreacted $Cr(NH_3)_2(NCS)_4^-$ as the tetramethylammonium salt and using the measured absorption of the filtrate at 303 mμ. The decrease in concentration of complex was then compared with the concentration of free thiocyanate as determined by the iron reagent.

For 6 hr, 1 day, and 4 days, the values of the former were 1.49, 8.0, and 28.8%, respectively, and the corresponding ratios of free thiocyanate to aquated complex were 1.50, 1.36, and 1.66, for an average of 1.5. The true aquation rate constant for the first stage is then $1.0 \times 10^{-4}/1.5$ or 6.7×10^{-5} min^{-1} at 23°.

B. Results. (1) $KCr(NH_3)_2(NCS)_4$. The central results, for 23° and at the natural pH of 5.3 to 5.5, are given in Table III. Each entry represents an independent run; the large number of entries for 545 mμ results from the choice of this wavelength as the one at which to make periodic reruns to check for any systematic drift in behavior of the equipment.

The effect of light intensity was small, as would be expected in a case of simple photoaquation. By using the Corning glass filter combination (CS 4-96, 3-72, 4-96, 1-69) a broad window centered at 505 mμ, with 52% transmission and a half-width of 80 mμ, was obtained, so that a tenfold increase in absorbed light intensity resulted. The 3% effect reported in Table III is within our experimental error.

As indicated by the marked entries in Table III, there was no noticeable effect on pH of quantum yields at 23°, so long as the solutions were acid. In alkaline solutions, however, the yield increased markedly, but it was found that the effect was independent of whether the addition of OH^- was before or after irradiation. Thus the primary photolysis step was not being affected, but only the degree to which hydrolysis of the primary product, presumably $Cr(NH_3)_2(NCS)_3(H_2O)$ occurred.

The results of some experiments at 545 mμ are summarized in Table IV. In each case, water solutions at pH 5.3 were photolyzed in the usual manner; then the pH was changed to the value in column 1 by the means indicated in column 2. After the stated times of standing, the amount of free thiocyanate ion was determined and the result reported as φ_{SCN} in column 4.

Table IV. Effect of pH on Quantum Yields for Thiocyanate Release by $KCr(NH_3)_2(NCS)_4$ at 23° and 545 mμ

pH	Attained by	Post-irradiation standing, hr	φ_{SCN}	φ_{SCN}/0.282
1.65	0.1 *N* H_2SO_4	1.8	0.278	0.99
5.2	. . .	2.5	0.300	1.06
5.6	Buffer	1.5	0.357	1.27
7.8	Buffer	1	1.06	3.76
12.6	0.1 *N* KOH	2	1.10	3.90

Line two of the table shows that there was a small increase in free thiocyanate on long standing of the photolyzed solution, but the main point is that any increase in alkalinity led, on standing, to increased free thiocyanate up to a maximum ratio of about 3.9 to that present immediately after the irradiation. Many more experiments were carried out than those reported in the table, and the terminal ratios were somewhat variable, ranging from 3.7 to 4.0 so that there was some irreproducibility in behavior. The matter is discussed further in section III.

The temperature dependence of φ_{SCN} was small, as shown in Table V. The table also includes the results of some further investigation of pH effects in that data both for solutions at the natural pH of 5.3–5.5 and 0.1 *N* in H_2SO_4 are given, along with the apparent quantum yields, φ_{OH}, when the irradiated solutions were made alkaline with 0.1 *N* KOH and allowed to stand 4 hr before thiocyanate analysis.

Table V. pH and Temperature Effects on φ_{SCN} for $Cr(NH_3)_2(NSC)_4$ at 545 mμ

Temp, °C	Solutions irradiated at pH 5.3–5.5			Irradiated solution 0.1 *N* in H_2SO_4		
	φ_{SCN}	φ_{OH}	$\varphi_{OH}/\varphi_{SCN}$	φ_{SCN}	φ_{OH}	$\varphi_{OH}/\varphi_{SCN}$
23	0.282	1.10	3.90	0.280	1.10	3.93
30	0.311[a]	1.18	3.80	0.297[a]	1.17	3.94
40	0.344[a]	1.24	3.60	0.314[a]	1.23	3.92
50				0.351[a]	1.37	3.84

[a] Average of two runs.

First, the temperature dependence of the quantum yield in 0.1 *N* H_2SO_4 was small; the apparent activation energy is 1.3 kcal/mole. Second, it will be noticed that in the case of the pH 5.3–5.5 solutions, the quantum yields rose more rapidly with temperature, but that the φ_{OH} values showed the same temperature dependence for both series. Finally, the ratio $\varphi_{OH}/\varphi_{SCN}$ remains close to 3.9 for the acid series, but decreases with increasing temperature for the series in which the irradiated solutions were at their natural pH. Evidently at this pH of 5.3–5.5 an increasing amount of secondary aquation occurs during the irradiation, which is largely suppressed if the irradiated solution is more acid.

As a further note on pH effects, another variation showed up with irradiations at 350 mμ. For these, at 23° and pH 5.6, φ_{SCN} was 0.388 and the ratio $\varphi_{OH}/\varphi_{SCN}$ was only 2.98, which means that 4/2.98 or 1.34 thiocyanates were released per chromium, as opposed to essentially one at the longer wavelengths. If the irradiated solution was 0.074 *N* in acid (nitric acid in this case), the value of φ_{SCN} dropped to 0.369, $\varphi_{OH}/\varphi_{SCH}$ was 3.34, and the ratio 4/3.34 indicates that 1.2 thiocyanates were released per chromium. This could be a matter of some secondary photolysis isnce if the φ_{SCN} values are divided by 1.34 and 1.20, respectively, the resulting quantum yields are about those obtained for the longer wavelengths. A similar result was found on irradiation at 316 mμ in that the value of φ_{SCN} not only dropped to 0.291, but $\varphi_{OH}/\varphi_{SCN}$ again was about 3.3, corresponding to 1.2 thiocyanates released per chromium. These points are discussed further in section III.

A few experiments were made to see if a highly paramagnetic ion, Mn^{+2}, might affect the quantum yield. With 1 *M* $Mn(NO_3)_2$, 0.1 *M* $H_2S_2O_4$, and 5 × 10^{-3} *M* complex, φ_{SCN} at 23° was 0.272 at 545 mμ (as compared to the 0.282 normal value). Similarly, no significant effect of urea was observed; φ_{SCN} was 0.284 for a solution at pH 5.5 and 1 *M* in urea. Two quantum yields were obtained for nonaqueous systems. For methanol solutions, φ_{SCN} was 0.201 both at 545 and 713 mμ, while in nitromethane, it was found to be 0.169 at 545 mμ (23° in both cases).

(2) $Cr(urea)_6Cl_3$. Our main body of results of the hexaurea system are given in Table VI for 22° and aqueous solutions at the natural pH of 3.9–4.1. As before, each entry represents an independent run.

The relatively large spread in quantum yields at 735 mμ may be due to the possibility that even though the work was all done under dim orange-red lighting, some variable amount of photolysis occurred during handling, which would make the most pronounced error in this case.

The temperature dependence of the photoaquation quantum yields was again small. For light of 628 mμ, 0.01 *M* solutions of complex at pH 3.9–4.1, and an absorbed light intensity of 16.5 × 10^{-9} einstein/sec, quantum yields of 0.115 and 0.117 were obtained at 30°, and of 0.135 and 0.137 at 40° (*vs.* 0.101 at 22°). The corresponding apparent activation energy is 3.0 kcal.

Some photoaquation quantum yields were also determined for $Cr(NCS)_6^{-3}$. These are summarized in

Table VI. Quantum Yields for Photoaquation of Cr(urea)$_6$ at 22° and pH 4.0

Wavelength, mμ	Extinction coeff, ε	Concn, $M \times 10^3$	Absorbed intensity, einsteins/sec $\times 10^9$	% photolysis/time, min	Quantum yield
452 (absorption max, 444 mμ)	37.1	13.0	7.17	0.36/30	0.0979
				0.38	0.103
			7.07	0.38	0.103
				0.36	0.0998
					Av. 0.101
520 (absorption min)	6.7	40.0	15.4	0.23/30	0.0890
				0.22	0.0874
			14.7	0.21	0.0849
					Av. 0.0871
585	31.6	15.0	14.9	0.39/20	0.0885
				0.40	0.0902
		20.0	14.2	0.27	0.0865
				0.27	0.0865
		15.0	14.4	0.39	0.0918
					Av. 0.0887
600	40.6	10.0	13.4	0.59/20	0.0987
				0.59	0.0987
				0.61	0.103
				0.60	0.101
			11.0	0.47	0.0957
					Av. 0.0994
628 (absorption max, 620 mμ)	45.5	10.0	18.4	0.85/20	0.104
				0.84	.0102
				0.82	0.101
			18.2	0.81	0.100
				0.81	0.100
			17.0	0.75	0.0994
					Av. 0.101
652	35.7	13.0	14.9	0.49/20	0.0960
				0.50	0.0981
				0.48	0.0939
			15.1	0.50	0.0970
				0.49	0.0948
					Av. 0.0960
676	23.4	20.0	17.0	0.35/20	0.0939
				0.36	0.0974
				0.34	0.0919
				0.35	0.0947
			15.9	0.33	0.0953
					Av. 0.0946
696	18.3	25.0	15.0	0.38/20	0.0955
				0.38	0.0960
				0.39	0.0964
					Av. 0.0950
735	4.5	50.0	22.7	0.28/30	0.0922
			22.9	0.29	0.0949
			22.6	0.31	0.102
			22.4	0.31	0.105
			21.9	0.26	0.0892
					Av. 0.0967

Table VII. The solutions were brought to pH 1.2 with 0.1 *N* H_2SO_4 or with HNO_3 to minimize the secondary aquation that occurred at higher pH values.

If the photolyzed solutions were made 0.1 *N* in KOH and allowed to stand for 1 hr, then added thiocyanate release occurred, with ratios of $\varphi_{OH}/\varphi_{SCN}$ which averaged 5.9. As with Reinecke's salt, we conclude than that only one thiocyanate is aquated in the primary step and that further release occurs only as a result of subsequent thermal hydrolysis reaction.

The hexathiocyanato system was considered for use in actinometry, since the quartet ligand field bands are at 421 and 567 mμ, *i.e.*, at somewhat longer wavelengths than for $Cr(NH_3)_2(NCS)_4^-$. However, the thermal aquation rate constant for thiocyanate release is 1.63×10^{-3} min^{-1} at 25°,[16] or some 15 times larger than that for $Cr(NH_3)_2(NCS)_4^-$, so that an inconveniently large thermal background reaction would be present.

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(16) To be compared to a value of 1.5×10^{-3} calculated from the data of N. Bjerrum, *Kgl. Danske Videnskab. Selskabs Skrifter, Naturvidenskab. Math. Afdel.*, [7] **12**, 147 (1915).

Table VII. Photoaquation of $K_3Cr(NCS)_6$ at 23°, pH 1.2

Wave-length, mμ	Extinction coeff, ε	Concn, $M \times 10^3$	Absorbed intensity, einstein/sec $\times 10^9$	% aquation time, min	Quantum yield
545	132	5.0	9.7	3.02/30	0.250
			8.8	2.80	0.256
			7.1	3.79/50	0.259
					Av. 0.255
600	108	5.0	14.8	5.02/30	0.274
			14.4	4.92	0.274
			14.1	5.00	0.268
				3.12/30	0.268
		10.0	14.4	2.40/30	0.268
					Av. 0.270

II. Chemical Actinometry with Aqueous $KCr(NH_3)_2(NCS)_4$ and $Cr(urea)_6Cl_3$

The procedures described in section I are here summarized in more compact form and from the point of view of using the two systems for chemical actinometry. A general procedure, suitable for a wide variety of geometrical arrangements, is that of the equivalent optical density method.[17,18]

A. Aqueous $KCr(NH_3)_2(NCS)_4$. Recrystallized $KCr(NH_3)_2(NCS)_4$ should be prepared from the commercial Reinecke's salt, as described in section IA, and solutions, preferably of sufficient concentration to absorb all incident light (to avoid transmission corrections[19]), should be made up at the time of use. The solutions can be slightly acidified with sulfuric acid or may be left at the natural pH of 5.3–5.5. Filtration of solutions more than 0.01 M is desirable although the actual effect on quantum yield is small as the scattered light from suspended impurities is still largely absorbed. The concentration of released thiocyanate is determined by mixing an aliquot of the solution with a known but not less than threefold larger volume of iron reagent. This last consists of 0.1 M $Fe(NO_3)_3 \cdot 9H_2O$ in 0.5 M $HClO_4$.

A parallel dark run should always be made, and the net or photoreleased thiocyanate determined by differential spectrophotometry at 450 mμ, using ε 4.3×10^3. The concentration of photoreleased thiocyanate times the volume of irradiated solution, divided by the appropriate quantum yield figure from Table III then gives the absorbed intensity in einsteins for the period of the irradiation. If light intensities are low, then all operations should be carried out in dim orange-red light to minimize the correction for background photolysis. The solution being irradiated should be stirred either continuously or at intervals not larger than corresponding to about 0.5% photolysis, and the total amount of photolysis should not exceed 10%.

B. Aqueous $Cr(urea)_6Cl_3$. $Cr(urea)_6Cl_3$ is prepared and dried as described in section IA. To minimize correction for transmitted light, solutions, made up fresh at the time of use, should be sufficiently concentrated that complete absorption will occur. In the analysis for photolyzed complex, it is important that the precautions as to concentration levels that are noted in section IA be followed.

C. Comparison of the Two Systems. The $KCr(NH_3)_2(NCS)_4$ system is the simpler of the two to use for actinometry. The compound (Reinecke's salt) is commercially available, the quantum yields are threefold higher (and may be magnified by a further factor of 3 if the added detail of making the irradiated solutions alkaline and allowing them to stand for 2 hr before analysis is included). The analysis is much more convenient and rapid. However, the extinction coefficients fall off rapidly for wavelengths longer than 600 mμ. The added precautions involved in working with the much more concentrated solutions required (and even so having to correct for incomplete light absorption) may make the two systems about comparable in convenience of use between 600 and 735 mμ.

III. Discussion

The photochemistry of aqueous Cr(III) complexes so far studied (see ref 1, particularly 1c and 1f) shows several consistencies. The photolytic reaction is always one of aquation, or is aquation related as in the case of photoracemization[1d] and photoisomerization.[1f] By contrast, Co(III) complexes tend to show varying proportions of photooxidation–reduction and photoaquation according to the wavelength of irradiating light.[1b] Further, the quantum yields for Cr(III) species are often nearly wavelength independent, although different systems may have markedly different temperature dependencies of quantum yield.

The first generality is explainable if one assumes that photooxidation–reduction occurs largely to the extent that charge-transfer character (of ligand-to-metal type) is present in the absorption band in question.[1b] Thus, unlike the situation with many Co(III) complexes, the visible absorption bands for Cr(III) complexes appear to be mainly ligand field in nature, hence the lack of photooxidation–reduction on irradiation with light of wavelength corresponding to these bands.

We plan to discuss the mechanism of Cr(III) photolysis in more detail in a later paper. However, an important consideration in such discussion is the degree to which photochemical behavior is wavelength dependent, and our present observations in this respect are summarized below.

First, it might be noted that our quantum yields do show small variations with wavelength, and ones which

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[17] D. H. Volman and J. C. Chen, *J. Am. Chem. Soc.*, **81**, 4141 (1959).

[18] I. M. Claesson, *Arkiv Kemi*, **10**, 1 (1956).

[19] Such correction will be unavoidable with light above 600 mμ.

we feel may be real. In the case of $Cr(NH_3)_2(NCS)_4^-$, there is a small, steady drop in quantum yield with increasing wavelength, while for $Cr(urea)_6^{+3}$ the quantum yield drops from 0.10 at the 444-mμ absorption maximum to 0.087 at the 520-mμ minimum, and rises to 0.10 at the second maximum at 620 mμ. Such variations could be ascribed, in terms of the doublet mechanism,[2a,b] to variations in the efficiency of conversion from the quartet excited state involved to the doublet state. If the efficiency can vary, it must be less than unity, so that quantum yields should rise when light in the doublet absorption band region is used. As will be seen below, this appears not to be the case.

There are, furthermore, some indications of mechanism complexity in the case of $Cr(NH_3)_2(NCS)_4^-$, although the situation is less clear-cut than it was with *cis*-$Cr(en)_2(OH)_2^+$.[1f] It will be recalled that in the thermal aquation reaction, an average of 1.5 thiocyanates appear to be released per initial step, presumably because of a relatively rapid equilibrium between $Cr(NH_3)_2(NCS)_3(H_2O)$ and $Cr(NH_3)_2(NCS)_2(H_2O)_2^+$. Photoaquation yields only one thiocyanate per complex photolyzed, except at the higher temperatures, where the figure rises slightly. This difference in behavior could be thought merely to be due to the fact that the photolysis was relatively rapid compared to the thermal reaction so that secondary thermal processes did not have time to occur. However, there is some indication that the photoaquation product may be different from the thermal one. Thus in a thermal aquation run at 40° to a point where a 21% decrease occurred in the 520-mμ band, it was observed that neither it nor the 392-mμ band shifted in position; for this degree of aquation only a reduction in intensity could be seen. On the contrary, photolysis at 520 mμ to a 14% decrease in intensity of this band led not only to the decrease, but to a shift in band maximum to 525 mμ (and in the 392-mμ band, to a shift to 394 mμ). These were quite distinct effects, not due to secondary photolysis since the $\varphi_{\rm OH}$ value still corresponded to only one thiocyanate released per complex photolyzed.

A possible explanation is that, as with *cis*- and *trans*-$Cr(en)_2(OH)_2^+$, isomerization as well as aquation was occurring. A stereochemical analysis of the photolysis products might well show not only this but that the effect was wavelength dependent.

Furthermore, as noted in section I, irradiation at 350 mμ appeared to result in about 1.2 thiocyanates released per complex photolyzed. We cannot rule out secondary photoaquation here, but the possibility that a 20% onset of prompt double aquation was present should be considered. A further effect was observed at 316 mμ in that $\varphi_{\rm SCN}$ showed a drop. Some qualitative tests indicate that irradiation in this general wavelength region produces some free ammonia, so that the reduction in $\varphi_{\rm SCN}$ may reflect competition with a new mode of photolysis. At any rate we doubt that it is safe to assume that spectrospecific effects are absent merely because the present study was not particularly designed to look for them.

The absorption spectra in the doublet region for $Cr(NH_3)_2(NCS)_4^-$, $Cr(urea)_6^{+3}$, and $Cr(NH_3)_6^{+3}$ are displayed in Figure 4 so as to allow a clear showing of the degree to which these bands stand out from what is presumably the tail of the nearest quartet band. With both the $Cr(NH_3)_6^{+3}$ and the $Cr(NH_3)_2(NCS)_4^-$ systems it is necessary to take pains to have very pure and dust-free solutions to avoid a high background of simple scattering; we believe our spectra not to be significantly perturbed in this respect.

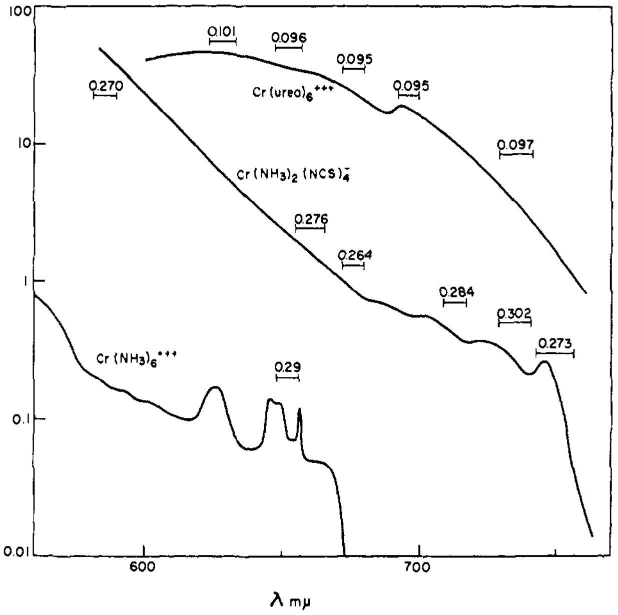

Figure 4. Absorption spectra and quantum yields in the doublet band region.

The quantum yield data for the first two complexes are given in Tables V and VI. For $Cr(NH_3)_6^{+3}$, we obtained a value of 0.26 at 22°, using light of 452 mμ, 0.01 *M* complex at pH 5.2, and a 15-min irradiation time at 7.7 × 10^{-9} einstein/sec light intensity (and 2.22% photolysis). This agrees reasonably well with the value of 0.32 reported by Edelson and Plane.[2b] At 652 mμ, our value at 22° is 0.29, or virtually the same. Here, 0.050 *M* complex was used, and a 150-min irradiation time at 1.69 × 10^{-9} einstein/sec absorbed (and 1.03% photolysis). This last value contrasts sharply with that of 1.3 reported for 650 mμ by the above authors. However, for lack of a chemical actinometer operative at that wavelength, they were forced to rely on the manufacturers apparently low estimate of relative light output by their lamp.

These various quantum yields are entered in Figure 4, and it is seen that for $Cr(NH_3)_2(NCS)_4^-$ small variations do occur, but within our experimental error. There is no indication of any change in quantum yield in the case of the hexaurea complex, and, as mentioned above, the rise from 0.26 to 0.29 in the case of the hexaammine complex is of marginal significance. It might be noted that for both $Cr(NH_3)_2(NCS)_4^-$ and $Cr(urea)_6^{+3}$ results are reported for wavelengths beyond the longest wavelength doublet feature.

Acknowledgments. The standardization of the $KCr(NH_3)_2(NCS)_4$ and $Cr(urea)_6^{+3}$ systems for use in chemical actinometry was supported by a grant from the National Science Foundation. The additional investigations designed to add information concerning the mechanism of the photolysis of Cr(III) complexes were supported by the Atomic Energy Commission, under Contract AT (11-1)-113. E. E. W. wishes to acknowledge a travel grant from the Deutscher Akademischer Austauschdienst. The authors further are indebted to Mr. R. Hahn for assistance in several of the preparations of complex compounds. We are also very grateful to Dr. G. M. Wyman for his encouragement of this work.

An Improved LCAO–MO–SCF π-Electron Method.
I. Hydrocarbons

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Abstract: A modified semiempirical π-electron method based on an LCAO–MO–SCF formulation is presented. This method differs from conventional Pariser–Parr–Pople SCF calculations in that the core integrals over atomic orbitals involve orthogonalized Slater-type orbitals. Furthermore, the one-electron core operators are expressed in such a manner that core parameters depend only on the kind of atom involved and the distance to its nearest neighbors. The parameters required for hydrocarbon molecules are systematically derived from ethylene and benzene as reference molecules. The parameters are tested by calculating several properties of naphthalene, anthracene, phenanthrene, and a series of polyenes of the type H—(CH═CH)$_n$—H. This test constitutes an attempt, therefore, to derive a single set of parameters common to both aromatics and polyenes. Comparison of the results with those achieved by Pariser–Parr–Pople calculations and with experiment indicate that an improvement over conventional calculations has been achieved.

There have been a number of basic parameters, and methods of obtaining parameters, suggested for use in semiempirical π-electron calculations.[1,2] If one selects a particular property and molecule (or restricted class of molecules), it has been possible to obtain reasonable agreement with experiment by the proper choice of the parameters that enter with the LCAO–MO–SCF method. However, it has been noted repeatedly that those parameters applicable to some property and molecules may not be readily generalized to other situations. For this reason the method, the parameters, and the results are often treated with suspicion.

In this investigation we propose to examine the parameter problem using both aromatic hydrocarbons and linear conjugated polyenes as test systems. We wish to show that it is possible to develop an internally consistent method that does lead to results that may be used with confidence. During the course of this investigation, it was recognized that the conventional method for dealing with the core integrals was inadequate. Thus a new method of evaluation will be considered as well.

Method

In this section the important features of the present SCF method are outlined.

1. The π-electron approximation is adopted.
2. The molecular orbitals are taken as a linear combination of Löwdin atomic orbitals. The Löwdin orbitals[3] are related to Slater-type orbitals (S.T.O.'s) as shown in eq. 1, where λ is the array of Löwdin

$$\lambda = \chi \mathbf{S}^{-1/2} \tag{1}$$

orbitals, χ is the array of S.T.O.'s, and $\mathbf{S}^{-1/2}$ is derived from the overlap matrix over S.T.O.'s.

3. The Hamiltonian operator is written as

$$H = \sum_i H_{\text{core}}(i) + \sum_{i>j} e^2/r_{ij} \tag{2}$$

The operators $H_{\text{core}}(i)$ are further expanded using the Goeppert-Mayer and Sklar[4] approximation. In its usual form the Goeppert-Mayer and Sklar expansion of $H_{\text{core}}(i)$ leads to the following expression for $\langle \psi_p(i) | H_{\text{core}}(i) | \chi_q(i) \rangle$. For $p = q$

$$H_{pp} = \langle \chi_p(i) | T(i) + U_p^+(i) | \chi_p(i) \rangle - \sum_{r \neq p} (pp/rr) + \sum_{r \neq p} (U_r^0 : pp) \tag{3}$$

and for $p \neq q$

$$H_{pq} = \langle \chi_p(i) | T(i) + U_q^+(i) | \chi_q(i) \rangle - \sum_{r \neq q} (pq/rr) + \sum_{r \neq q} (U_r^0 : pq) \tag{4}$$

In eq. 3 and 4 the integrals (pp/rr), more compactly designated γ_{pr} below, and (pq/rr) are two- or three-center, two-electron repulsion integrals (over S.T.O.'s). The integrals $(U_r^0 : pp)$ and $(U_r^0 : pq)$ are neutral atom penetration integrals including hydrogen atoms.

Equation 3 can be simplified by neglecting those neutral atom penetration integrals where r refers to those carbon and hydrogen atoms which are nearest neighbor to atom p. For a nonbridge, nonterminal

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