Table I. Equilibrium Constants and Heat for the Reaction $C_2F_4(g) = 2CF_2(g)$

Temp, °K	$-\log K_{eq}$	$-\Delta[(G^\circ - H^\circ_{298})/T]$, cal deg^{-1} mole^{-1}	ΔH°_{298}, kcal mole^{-1}
1220	4.28	43.42	76.9
1230	4.07	43.46	77.6
1244	3.98	43.56	76.8
1217	4.21	43.40	76.3
1205	4.33	43.33	76.1
1193	4.58	43.26	76.6
1173	4.74	43.17	76.1
1162	4.92	43.12	76.3
1151	5.02	43.06	76.0
1138	5.18	43.02	75.9
1127	5.33	42.94	75.9
$\Delta H^\circ_{298}(\text{av}) = 76.5 \pm 0.2$ kcal mole^{-1}			

Discussion

By using the mean value of the second- and third-law heats of reaction, $\Delta H^\circ_{298} = 76.3 \pm 3.0$ kcal mole^{-1}, together with the heat of formation of C_2F_4, $\Delta H_f{}^\circ{}_{298} = -155.0 \pm 2.0$ kcal mole^{-1},[6] one obtains -39.3 ± 3 kcal mole^{-1} for $\Delta H_f{}^\circ{}_{298}(CF_2)$. This value is very close to second-law values obtained in the shock-tube experiments[10,11] and also agrees, within the limits of experimental error, with Pottie's results.[8] Thus, on the basis of existing data, one confidently chooses $\Delta H_f{}^\circ{}_{298}[CF_2(g)] = -39 \pm 3$ kcal mole^{-1} and notes that the agreement of various experimental approaches validates the assumption of equilibrium in the various systems.

Table II gives currently accepted heats of formation of various fluorocarbon species, and Table III summarizes the dissociation energies of different carbon-fluorine bonds.

Table II. Heats of Formation of CF_n Species ($n = 1, 2, 3, 4$)

Species	$\Delta H_f{}^\circ{}_{298}$, kcal mole^{-1}	Species	$\Delta H_f{}^\circ{}_{298}$, kcal mole^{-1}
CF_4	-223.0 ± 1.0[a] -222.87 ± 0.38[b]	CF_2 CF	-39 ± 3[d] 49.2 ± 8.7[e]
CF_3	-115.9 ± 2.5[c]		

[a] J. L. Wood, R. J. Lagow, and J. L. Margrave, *J. Chem. Eng. Data*, **12**, 2 (1967). [b] E. S. Domalski and G. T. Armstrong, *J. Res. Natl. Bur. Std.*, **71A**, 105 (1967). [c] Reference 6. [d] This work and ref 8, 10, and 11. [e] Reference 11; an alternative interpretation of the CF spectra was used for several years to derive $D(CF) = 115$ kcal mole^{-1} which is close to the average bond energy in CF_4; see ref 6.

Table III. Carbon-Fluorine Bond Strengths

Bond	D°_{298}, kcal mole^{-1}	Bond	D°_{298}, kcal mole^{-1}
CF_3-F	126.0[a]	CF-F	107.4,[a] 120[b]
CF_2-F	95.5[a]	C-F	140.6,[a] 132[b]

[a] Calculated from the respective heats of formation listed in Table II and by using values $\Delta H_f{}^\circ{}_{298}(F) = 18.86$ kcal mole^{-1} and $\Delta H_f{}^\circ[C(g)] = 170.9 \pm 0.5$ kcal mole^{-1} (ref 6). [b] Data reported by Thrush and Zwolenik[5] from predissociation in the spectra of CF_2 and CF.

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Chemistry of ^{38g}Cl Recoils in Neutron-Irradiated Crystalline $KClO_2$, $KClO_3$, and $KClO_4$

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Abstract: The distribution of recoil 37.5-min ^{38g}Cl among the chlorine valence states following the $^{37}Cl(n,\gamma)^{38}Cl$ reaction at 35° in crystalline $KClO_2$, $KClO_3$, and $KClO_4$ was measured. Anion-exchange column separations performed on aqueous solutions of the irradiated solids showed that radiochloride was the principal species formed. The production of $^{38}ClO_2^-$ and of $^{38}ClO_2$ was observed for the first time, as was the formation of $^{38}ClO_3^-$ in $KClO_2$ and of $^{38}ClO_4^-$ in $KClO_3$. The generation of small amounts of radioperchlorate ion in irradiated $KClO_4$ was confirmed. Radiohypochlorite appeared to be formed in very small yield, if at all. Comparisons of the relative yields of the chlorine valence states produced by ^{60}Co γ-radiation with those for recoil radiochlorine indicated that the rupture of all the Cl-O bonds in the target anion is much more probable in the "hot-atom" than in the radiation chemical process.

The chemistry of ^{38g}Cl recoil atoms formed by neutron irradiation of chlorine oxyanions in crystals has been the subject of recent investigations[1,2] which have generally confirmed and extended the findings of early research.[3,4] The valence states in which radiochlorine has been observed are chloride, chlorate, and perchlorate. However, few generalizations about yields can be made, and significant discrepancies between these reports are evident. It has seemed worthwhile, therefore, to conduct additional research to determine states of chemical combination of recoil radiochlorine generated by neutron irradiation of crystalline $KClO_2$, $KClO_3$, and $KClO_4$. The possibility that ^{38}Cl might be found in oxidation states other than those reported was

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[1] M. Vlatković and A. H. W. Aten, Jr., *J. Inorg. Nucl. Chem.*, **24**, 139 (1962).

[2] N. K. Aras, B. Kahn, and C. D. Coryell, *ibid.*, **27**, 527 (1965).

[3] W. F. Libby, *J. Am. Chem. Soc.*, **62**, 1930 (1940).

[4] K. J. McCallum and O. G. Holmes, *Can. J. Res.*, **29**, 691 (1951).

suggested by studies on the radiolysis of crystalline $KClO_3$,[5-7b] $KClO_4$,[8,9] and $NaClO_4$[10] by X-rays and ^{60}Co γ-rays where, in addition to chloride and oxygen gas, chlorite, chlorine dioxide, hypochlorite, and perchlorate have been observed.

Electron spin resonance studies with γ- and X-ray irradiated crystalline $NaClO_3$,[11] $KClO_3$,[12] $Ba(ClO_3)_2$,[12] and $KClO_4$[13-16] have revealed several paramagnetic centers which are stable at room temperature. In $NaClO_3$ and $KClO_3$ the species ClO_2 and ClO_3 have been identified. The former paramagnetic radical which is formed at room temperatures and below appears to be trapped in a ClO_3^- vacancy in the crystal. The ClO_3 radical appears stable at room temperature; its resonance lines may be annealed completely by heating the irradiated crystal at 195° for 1 hr and then regrown by subsequent irradiation at room temperature. The paramagnetic centers in irradiated $KClO_4$ have been identified as ClO_2, ClO_3, and ClO_4. The first two radicals are reasonably stable at room temperature but the latter exists only at 77°K.

Experimental Section

Materials. Reagent grade $KClO_3$ and $KClO_4$ were employed without further purification. The $KClO_2$ was prepared from $NaClO_2$[17] by methods to be described elsewhere.[18] The final purified crystalline product contained less than 1% chloride as determined by argentiometric analysis and $\leq 0.3\%$ chlorate.

Neutron Irradiations. Approximately 5–10 mg of the crystalline salts were irradiated in air for 2 min at the terminus of the pneumatic transfer tube in the Oak Ridge Research Reactor (ORR), a heterogeneous, light-water moderated, uranium–aluminum alloy fueled tank-in-pool facility where the thermal neutron flux at a power level of 30 MW was 4.9×10^{13} cm^{-2} sec^{-1} and the cadmium/gold/cadmium ratio was 2.6. The radiolysis rate at this position measured with $^7LiBrO_3$ was 24.5×10^{-3} mole of BrO_3^- decomposed per mole of $^7LiBrO_3$ per hour. This decomposition corresponds to a dose rate of 3.9×10^{20} eV g^{-1} min^{-1} assuming $G(-BrO_3^-) = 0.47$ as found in earlier research[19] with nuclear reactor radiations. The irradiated crystals were analyzed as soon as possible after removal from the reactor because of the short ^{38}Cl half-life.

Analysis of Irradiated Crystals. The distribution of 37.5-min ^{38g}Cl among the chlorine valence states was determined by analysis of alkaline aqueous solutions of the neutron-irradiated crystals at room temperature. An anion-exchange chromatographic method was employed with bicarbonate, nitrate, and tetrafluoroborate, BF_4^-, solutions as eluents. The dimensions of the ion-exchange column and other procedural details have been given elsewhere.[20] Aqueous solutions of the irradiated salts were pretreated by passing them through shallow beds of potassium-form Dowex-50 cation exchanger to remove 12.5-hr ^{42}K activity, and an aliquot of the effluent was absorbed at the top of a bed of Dowex-1 anion exchanger. Typical radiochromatograms showing the anionic species are given in Figures 1–3. Complete separations were obtained in 90 min or less. The γ-ray activities in the peak volumes were measured in a 4π geometry ionization chamber and compared with the total γ activity in the entire volume collected in the separation.

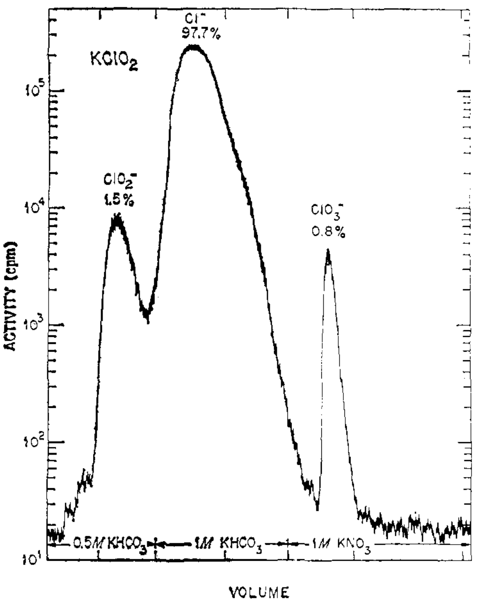

Figure 1. Anion-exchange chromatographic separation of 37.5-min ^{38}Cl activity in neutron-irradiated crystalline $KClO_2$.

γ-Ray spectra emitted by the peak fractions were measured with a 3 × 3 in. (Na + Tl)I crystal connected with a 400-channel pulse height analyzer. Only photopeaks characteristic of ^{38g}Cl were observed. Measurements of the decay of the γ activity in the column fractions gave a pure 37.5-min half-life.

Chromatographic experiments performed with solutions of irradiated KCl established that the dominant activity observed in the separations was associated with chloride ion. The identity of the ClO_2^- ion peak was determined by dissolving irradiated $KClO_3$ in 0.1 *M* bicarbonate solution containing $NaAsO_2$ and OsO_4 as a redox catalyst and subjecting the solution to a chromatographic analysis. The peak observed in the absence of reducing agent which was assumed to be caused by ClO_2^- had disappeared, as expected, and the amount of activity in the Cl^- fraction was increased by *ca.* 3% which was approximately the yield of ClO_2^- activity in the untreated solution.

An indirect test was made for the presence of $^{38}ClO^-$ in irradiated $KClO_3$. Arsenite ion, AsO_2^-, in alkaline aqueous media will reduce hypochlorite rapidly and quantitatively to Cl^- ion while chlorite is reduced only very slowly in the absence of a catalyst. Therefore, neutron-bombarded $KClO_3$ was dissolved in 0.1 *M* bicarbonate solution containing $NaAsO_2$, and the mixture was subjected to a chromatographic analysis. If $^{38}ClO^-$ had been present, the amount of $^{38}Cl^-$ found should have been increased over that obtained when irradiated $KClO_3$ was dissolved in 0.1 *N* HCO_3^- solution without AsO_2^- ion. Actually, the amount of $^{38}Cl^-$ was virtually the same in both analyses, suggesting that the yield of $^{38}ClO^-$, if it was formed at all, was less than 0.2%.

Tests were made to prove that the ^{38g}Cl activity found in the ClO_2^- and ClO_3^- ions did not originate from isotopic exchange reactions with $^{38}Cl^-$ or $^{38}ClO^-$. Inactive $KClO_2$ or $KClO_3$ was dissolved in alkaline aqueous solutions containing irradiated KCl, and the mixtures were subjected to an anion-exchange separation. No radiochlorine activity was found at the volume corresponding to the appearance of ClO_3^- ion in the effluent, demonstrating the absence of an exchange reaction between $^{38}Cl^-$ and ClO_3^- ions in solution. In a mixture with initially inactive $KClO_2$, however, a small $^{38}ClO_2^-$ peak was observed which contained *ca.* 0.1% of the total γ activity. This result indicated that a small, almost negligible exchange of activity between $^{38}Cl^-$ and ClO_2^- ions had occurred. The foregoing observations are in agreement with the report[21] that, except for the exchange between ClO_2 and ClO_2^-

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(5) H. G. Heal, *Can. J. Chem.*, 37, 979 (1959).

(6) A. S. Baberkin, "The Action of Ionizing Radiation on Inorganic and Organic Systems," Academy of Science, USSR Press, Moscow, 1958, p 187.

(7) (a) C. E. Burchill, cited by P. F. Patrick and K. J. McCallum, *Nature*, **194**, 766 (1962); (b) *J. Phys. Chem.*, 71, 4560 (1967).

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(18) L. C. Brown and G. E. Boyd, to be submitted for publication.

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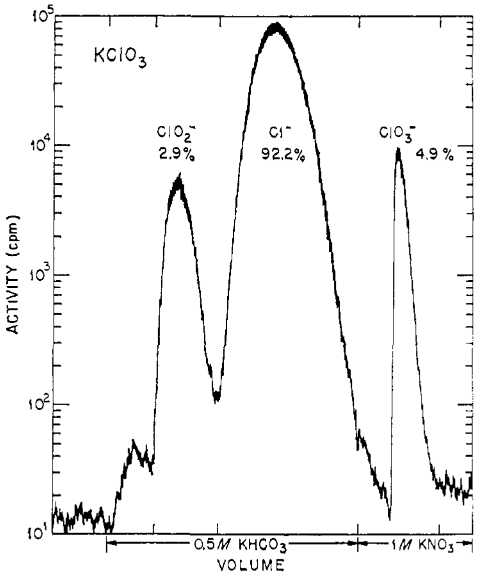

Figure 2. Anion-exchange chromatographic separation of 37.5-min ^{38}Cl activity in neutron-irradiated crystalline $KClO_3$ (small peak at lower left believed to be $^{38}ClO_2$). Elution with 1 *M* $NaBF_4$ solution gave a $^{38}ClO_4^-$ peak, not shown, following the $^{38}ClO_3^-$ peak. (The $^{38}ClO_4^-$ was present in *ca.* 0.05% yield.)

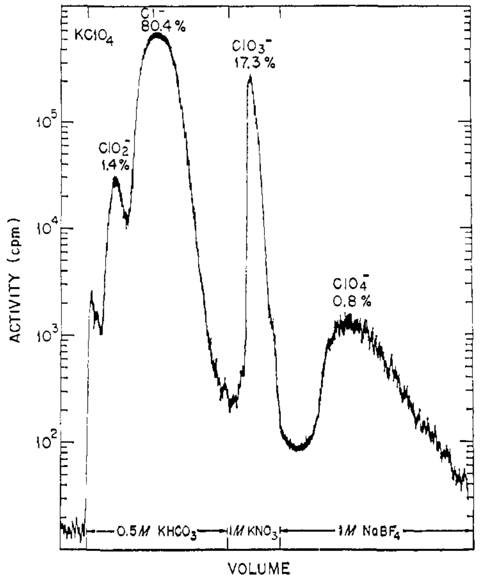

Figure 3. Anion-exchange chromatographic separation of 37.5-min ^{38}Cl activity in neutron-irradiated $KClO_4$ (small peak at lower left believed to be $^{38}ClO_2$).

ion which is rapid, the isotopic exchange rates of all the chlorine oxidation states in alkaline solutions are very small. The rate of exchange of ^{36}Cl between ClO_3^- and ClO_4^- ions in aqueous solution at room temperature has been demonstrated to be extremely small.[22]

A search was made for $^{38}ClO_2$ in neutron-irradiated $KClO_3$. The salt was dissolved in a neutral aqueous solution containing small amounts of "carrier" ClO_2[23] together with Cl^- and ClO_4^- ions as "hold-back carriers." The mixture was extracted four times with pure CCl_4, and the phases were separated by centrifugation. The combined CCl_4 extracts were washed twice with aqueous 0.1 *N* $NaAsO_2$ solution which acted to reduce ClO_2 to Cl^- ion and to transfer all the radioactivity from the organic to the aqueous phase. The activity in this aqueous phase was compared with a suitable aliquot of the initial solution of irradiated salt. A yield of 3.6% for $^{38}ClO_2$ + $^{38}ClO_2^-$ was found.[24] Independent measurements (*cf.* Table I) showed the yield of $^{38}ClO_2^-$ ion to be 2.9 ± 0.1%; hence the yield of $^{38}ClO_2$ was *ca.* 0.7%. The relatively very small, unlabeled initial peak that may be seen in Figures 2 and 3 quite possibly should be assigned to $^{38}ClO_2$. This peak disappeared when AsO_2^- was added to the initial solution of irradiated salt.

Radiolysis Measurements. Radiolytic decomposition of crystalline $KClO_3$ by ^{60}Co γ-rays was effected at *ca.* 35° in a constant-geometry arrangement.[25] The dose rate in water measured with a Fricke dosimeter solution was 1.03×10^{18} eV g^{-1} min^{-1}. Purified $KBrO_3$ was irradiated simultaneously and served as a monitor for the $KClO_3$ decompositions. Measurements of the yields of Cl^-, ClO^-, and ClO_2^- ions and the total decomposition of chlorate ion were performed with analytical procedures adapted from those used in studies on the radiolysis of the alkali metal bromates.[26,27] The following "100-eV yields" were obtained for a dose of 1.066×10^{23} eV (mole of $KClO_3$)$^{-1}$: $G(-ClO_3^-) = 3.95$; $G(Cl^-) = 1.10$; $G(ClO^-) + G(ClO_2) = 0.58$; $G(ClO_2^-) = 2.37$; and $G(ClO_4^-) = 1.09$. The sum, $G(Cl^-) + G(ClO^-) + G(ClO_2) + G(ClO_2^-)$, was 4.05, in fair agreement with the experimental value for $G(-ClO_3^-)$. Our values for $G(ClO_4^-)$ and $G(ClO^-) + G(ClO_2)$ agree well with those recently published by Burchill, Patrick, and McCallum.[7b] However, our value for $G(Cl^-)$ is distinctly lower than that by the latter authors, while our $G(ClO_2^-)$ is slightly higher. The sum, $G(Cl^-) + G(ClO^-) + G(ClO_2) + G(ClO_2^-)$, from the data of McCallum and coworkers is 4.19.

The salt $KBrO_3$ appeared significantly more stable than $KClO_3$ and moreover showed widely differing yields for homologous products. Thus, for a dose of 4.88×10^{23} eV (mole of $KBrO_3$)$^{-1}$ $G(-BrO_3^-) = 1.16$, $G(Br^-) = 0.61$, $G(BrO^-) + G(BrO_2) = 0.29$, and $G(BrO_2^-) = 0.21$.

Experimental Results and Discussion

Chemical Identities and Yields of Recoil Radiochlorine. The results from the chromatographic analyses performed on the neutron-irradiated oxychlorine anions are summarized in Table I. Radiochlorine was observed in five valence states, namely as Cl^-, ClO_2^-, ClO_3^-, and ClO_4^- ions and as ClO_2. The species $^{38}ClO_2^-$ and $^{38}ClO_2$ were observed for the first time as was the production of $^{38}ClO_3^-$ in $KClO_2$ and of $^{38}ClO_4^-$ in $KClO_3$. No evidence was obtained for the occurrence of either $^{38}ClO^-$ or $^{38}ClO_3$ possibly because of their thermal instability.

The yield of radiochloride was always the largest, even in $KClO_4$, while the yield of ClO_2^- was approximately independent of the target anion. Retention of ^{38}Cl by the target oxyanion was relatively small but finite in all the salts. Its value for $KClO_3$, $R(^{38}ClO_3^-) = 5.1 \pm 0.1\%$, is in fair agreement with the reports by Vlatković and Aten[1] and by Aras, Kahn, and Coryell,[2] but it is definitely larger than the 1.5% found by McCallum and Holmes.[4] The yield, $R(^{38}ClO_3^-) = 16.1 \pm 0.1\%$, of radiochlorate in $KClO_4$ is in good agreement with Aras, *et al.*,[2] but is larger than the value of *ca.* 10.8% by Vlatković and Aten.[1] The report[2] that small amounts of $^{38}ClO_4^-$ are formed in $KClO_4$ (*i.e.*, finite retention) was confirmed. It is of interest to note that in several instances small amounts of ^{38}Cl were found combined in an oxyanion with one more oxygen than the target anion: *i.e.*, approximately 0.8%

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(21) H. Dodgen and H. Taube, *J. Am. Chem. Soc.*, **71**, 2501 (1949).

(22) D. A. Lee, *ibid.*, **76**, 2590 (1954).

(23) Chlorine dioxide was prepared following the method outlined in the "Handbook of Preparative Inorganic Chemistry," Vol. I, 2nd ed, G. Brauer, Ed., Academic Press Inc., New York, N. Y., 1963, pp 301-302.

(24) The carrier ClO_2 was assumed to have exchanged rapidly and completely with the $^{38}ClO_2^-$ present in the initial solution (*cf.* ref 21).

(25) C. J. Hochanadel and J. A. Ghormley, *Radiation Res.*, **16**, 653 (1952).

(26) G. E. Boyd, E. W. Graham, and Q. V. Larson, *J. Phys. Chem.*, **66**, 300 (1962).

(27) J. W. Chase and G. E. Boyd, *ibid.*, 70, 1031 (1966).

Table I. Yields of Radiochlorine Species in Neutron-Irradiated Crystals Containing Chlorine Oxyanions (%)

$R(\mathrm{Cl}^-)$	$R(\mathrm{ClO_2}^-)$	$R(\mathrm{ClO_3}^-)$	$R(\mathrm{ClO_4}^-)$	Eluents in anion-exchange separation
			$\mathrm{KClO_2}$	
97.7	1.5	0.8	...	0.5 M $\mathrm{HCO_3}^-$, 1.0 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
98.0	1.3	0.7	...	0.5 M $\mathrm{HCO_3}^-$, 1.0 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
98.3	1.0	0.7	...	0.5 M $\mathrm{HCO_3}^-$, 1.0 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
98.4	1.1	0.5	...	0.5 M $\mathrm{HCO_3}^-$, 1.0 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
97.9	1.2	0.9	...	0.5 M $\mathrm{HCO_3}^-$, 1.0 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
98.5	1.0	0.5	<0.05	$\mathrm{AsO_2}^-$, 0.5 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
			$\mathrm{KClO_3}$	
93.0	1.9	4.9	...	1 M $\mathrm{HCO_3}^-$, 2 M $\mathrm{HCO_3}^-$
92.2	2.9	4.9	...	0.5 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
91.1	2.9	5.5	...	0.5 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
92.2	2.8	5.0	...	0.5 M $\mathrm{HCO_3}^-$, 2 M $\mathrm{HCO_3}^-$
92.1	2.9	5.0	...	0.1 M $\mathrm{NO_3}^-$, 2 M $\mathrm{NO_3}^-$
95.6	0.0	4.4	...	($\mathrm{AsO_2}^-$ + $\mathrm{OsO_4}$), 0.1 M $\mathrm{NO_3}^-$, 2 M $\mathrm{NO_3}^-$
92.2	2.2	5.7	0.05	$\mathrm{AsO_2}^-$, 0.5 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
			$\mathrm{KClO_4}$	
81.0	1.6	15.9	...	0.5 M $\mathrm{HCO_3}^-$, 1 M $\mathrm{NO_3}^-$
82.8	1.5	16.2	>0.2	0.1 M $\mathrm{NO_3}^-$, 1.0 M $\mathrm{NO_3}^-$, 2 M $\mathrm{NO_3}^-$
80.4	1.4	17.3	0.8	0.5 M $\mathrm{HCO_3}^-$, 1.0 M $\mathrm{NO_3}^-$, 1.0 M $\mathrm{BF_4}^-$

$^{38}\mathrm{ClO_3}^-$ was observed in $\mathrm{KClO_2}$ and ~0.05% $^{38}\mathrm{ClO_4}^-$ in $\mathrm{KClO_3}$.

This investigation has served to emphasize the complexity of the states of chemical combination of the recoil radiochlorine produced in oxyhalogen compounds. The origins of these valence states and the factors governing their relative yields will now be considered.

Origins of the Radiochlorine Valence States. Recoil $^{38g}\mathrm{Cl}$ is formed by neutron capture in stable $^{37}\mathrm{Cl}$ of 24.5% relative abundance in chlorine *via* two pathways (see eq 1). Because of the 86-fold larger cross-section

$$\begin{tikzcd} {}^{37}\mathrm{Cl}(n,\gamma) \arrow[r, "\sigma = 0.005b"] \arrow[d, "\sigma=0.43b"'] & {}^{38m}\mathrm{Cl} \arrow[dl, "\text{I.T.}\ 1\ \text{sec}"] \\ {}^{38g}\mathrm{Cl} \arrow[r, "37.5\ \text{min}", "\beta^-"'] & {}^{38}\mathrm{Ar}\ (\text{stable}) \end{tikzcd} \qquad (1)$$

for the production of $^{38g}\mathrm{Cl}$, most of the 37.5-min activity will be formed directly rather than by decay of the 1-sec isomeric state, $^{38m}\mathrm{Cl}$. Accordingly, mechanical recoil following neutron capture should be the principal mechanism for the breaking of chlorine–oxygen bonds, as virtually all of the neutron binding energy (6.11 MeV) is emitted as energetic γ-rays. The magnitude of the recoil energy will be sufficiently large that only a very small fraction of the Cl–O bonds will not be ruptured; if a single-capture γ-ray of 6.11 MeV is emitted, the energy imparted to the chlorine nucleus will be 526 eV. Even allowing for sharing with the internal degrees of freedom in a $\mathrm{ClO_4}^-$ ion, for example, the energy will still be many times greater than the Cl–O bond energy, 2.8 eV. The more probable decay of the excited compound nucleus formed by neutron capture is *via* a cascade of several γ-rays. However, even in this case the magnitude of the recoil energy will exceed the bond energy by an amount such that only a small percentage of the Cl–O bonds in an oxychlorine anion will survive the nuclear event unbroken. It will be assumed, therefore, that the target oxychlorine anions were totally disrupted and that the radiochlorine valence states observed were formed by subsequent reactions within the locally damaged crystal lattice.

The yield of radiochloride ions may be seen (Table I) to have increased as the number of Cl–O bonds in the oxychlorine anion decreased. This behavior is qualitatively consistent with the "ligand loss" hypothesis[3] which states that the chemical nature of the recoil will be determined by the distribution of bonding electrons in the molecule ion prior to neutron capture. However, the differences in $^{38}\mathrm{Cl}^-$ yields between $\mathrm{KClO_2}$, $\mathrm{KClO_3}$, and $\mathrm{KClO_4}$ are smaller than might be expected from the differences in the oxidation numbers of +3, +5, and +7, respectively, which imply that a wholesale transfer of electrons must occur to form chloride ion. The estimation of charge distribution in the oxychlorine ions is a difficult problem. However, recent applications of the ESCA shift method[28] to NaCl, $\mathrm{NaClO_2}$, $\mathrm{NaClO_3}$, and $\mathrm{NaClO_4}$ have indicated that the charges on chlorine in these crystalline compounds are −0.67, +0.20, +0.33, and +0.46, respectively. Thus, 0.87 to 1.13 electrons would need to be transferred from oxygen to chlorine to form chloride ion. It is reasonable also that the yield of radiochloride should decrease more rapidly than linearly with the charge on the chlorine in the target anion.

The data in Table I also reveal that for $\mathrm{KClO_3}$ and $\mathrm{KClO_4}$ the recoil yields follow the sequence $\mathrm{Cl}^- > \mathrm{ClO_3}^- \gg \mathrm{ClO_2}^- > \mathrm{ClO_4}^-$. The $^{38}\mathrm{ClO_2}^-$ ion may have been formed by back-reactions within the damaged region in the crystal lattice surrounding a $^{38}\mathrm{Cl}^-$ recoil. The low yield would be consistent with the observations of Vanden Bosch and Aten,[29] who were unable to detect any conversion of $^{38}\mathrm{Cl}^-$ ion added to crystalline $\mathrm{NaClO_3}$ to either chlorate or perchlorate ions on heating 30 min at 505°. The very small concentrations of $^{38}\mathrm{ClO_4}^-$ ions observed in neutron-irradiated $\mathrm{KClO_3}$ and $\mathrm{KClO_4}$ may have been formed by intercrystalline oxidation of $^{38}\mathrm{ClO_3}^-$ or by disproportionation. It is relevant in this connection to note the observation[30] that $^{36}\mathrm{ClO_3}^-$ dis-

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[28] K. Siegbahn, *et al.*, "Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, Sweden, 1967, p 96 ff.

[29] A. Vanden Bosch and A. H. W. Aten, Jr., *J. Am. Chem. Soc.*, 75, 3835 (1953).

solved in inactive crystalline $KClO_4$ reacts at 550° to give $^{36}ClO_4^-$ ion.

The cause for the relatively large yields of $^{38}ClO_3^-$ ion (Table I) remains unexplained. It seems unlikely that this species is formed from recoil $^{38}Cl^-$ in the same manner as postulated for $^{38}ClO_2^-$ ion. If intercrystalline oxidation of radiochloride were the dominant solid-state reaction, the expected sequence of yields would be $Cl^- > ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$. In fact, however, the yield of $^{38}ClO^-$ appears to be quite small, and that for $^{38}ClO_2^-$ is less than that for $^{38}ClO_3^-$ in $KClO_3$ and $KClO_4$. The low yields of $^{38}ClO^-$ and $^{38}ClO_2^-$ ions may be a consequence of their instability, or, what amounts to the same thing, the relatively great stability of $^{38}ClO_3^-$ ion may be the reason for its higher concentration.

Yields of Chlorine Valence States in Hot-Atom and Radiation Chemical Processes. A general similarity exists in the pattern of "hot-atom" yields of chlorine valence states and the yields from radiolysis of the same crystalline salts by energetic ionizing radiations. In both cases the predominant species were the same. However, in the γ-radiolysis of $KClO_3$ and $KClO_4$ relatively much larger yields of less degraded oxychlorine anions are produced than in the decompositions following neutron capture (*cf.* Table II). The breaking of a single Cl–O bond, for example, was much more probable when the ClO_3^- or ClO_4^- ions were excited or ionized by γ-rays than when the nucleus of the chlorine atom was excited by neutron capture.

Table II. Relative Yields (%) of Chlorine Valence States Formed by Recoil and by γ-Radiolysis

Process	$R(Cl^-)$	$R(ClO^-)$	R (ClO_2^-)	R (ClO_3^-)	R (ClO_4^-)
		$KClO_3$[a]			
"Hot-atom"	92.1	...	2.8	5.1	*Ca.* 0.05
γ-Radiolysis	21.8	11.5	47.0	...	21.2
		$KClO_4$[b]			
"Hot-atom"	81.9	...	1.6	16.1	0.2
γ-Radiolysis	11.7	2.4	4.7	78.0	...

[a] $G(-ClO_3^-) = 3.95$. [b] Entries for $KClO_4$ radiolysis computed from G values in ref 9: $G_0(-ClO_4^-) = 3.83$.

The radiolytic also differs from the recoil process in that in the former the yields of decomposition products are strongly dependent on the nature of the cation in the crystalline salt. Thus, in the radiolysis of the alkali metal perchlorates[9] by ^{60}Co γ-rays, the percentages of Cl^- ion formed in the lithium, sodium, potassium, rubidium, and cesium salts are 3.2, 9.6, 11.8, 14.2, and 15.7, respectively, whereas the percentages of recoil $^{38}Cl^-$ formed in the lithium, sodium, and potassium perchlorates[2] are 84, 90, and 85, respectively. A more dramatic difference may be observed in the yields of perchlorate ion in $KClO_3$ (Table II) where γ-radiolysis produced over 20% ClO_4^- but only 0.05% $^{38}ClO_4^-$ was formed by neutron capture.

Thermal Annealing Mechanisms. An increase in the retention of ^{38g}Cl in ClO_3^- ion from 3.5 to 7.0% on heating irradiated $KClO_3$ at 350° has been reported.[1] This small change is consistent with the observation noted above that radiochloride is not readily converted to radiochlorate ion at this or at higher temperatures. The increase in $^{38}ClO_3^-$ can be accounted for by the thermal disproportionation of $^{38g}ClO_2^-$ ion according to

$$3ClO_2^- \longrightarrow 2ClO_3^- + Cl^-$$

The production of small amounts (*i.e.*, 1%) of $^{38}ClO_4^-$ and the nearly complete disappearance of $^{38}ClO_3^-$ ion observed by Aras, Kahn, and Coryell when $KClO_3$ was heated 20 min at 500° also may be explained on the basis of a solid-state thermal disproportionation reaction

$$4ClO_3^- \longrightarrow 3ClO_4^- + Cl^-$$

A brief study was made of the thermal annealing of the nonchloride ^{38}Cl activity in irradiated $KClO_2$. Vlatković and Aten[1] have observed what they term "inverse" thermal annealing when irradiated $NaClO_2$ was heated at 100 or 154°, and they have suggested that most of the activity in the $ClO^- + ClO_2^- + ClO_3^-$ fraction they measured was present as $^{38}ClO^-$ ion and that this decomposed on heating. We have analyzed irradiated $KClO_2$ and irradiated and heated $KClO_2$ (*i.e.*, 20 min at 200°) chromatographically and have observed significant changes in the relative amounts of $^{38}ClO_2^-$, $^{38}Cl^-$, and $^{38}ClO_3^-$ ions (*cf.* Figure 1). On heating, the yield of $^{38}ClO_2^-$ decreased from 1.2 to 0.08%, while the yields of $^{38}Cl^-$ increased from 97.9 to 98.2% and of $^{38}ClO_3^-$ from 0.9 to 1.7%. These observations indicate that a significant decomposition of the $KClO_2$ occurred and that a mild heat treatment induced a solid-state oxidation reaction to form $^{38}ClO_3^-$.

A test for $^{38}ClO^-$ ion in the irradiated $KClO_2$ was made by pretreatment of the aqueous solution of the crystals with sufficient $NaAsO_2$ to convert all the hypochlorite to chloride: the yield of $^{38}Cl^-$ increased from 98.0 to 98.6% while the yield of $^{38}ClO_2^-$ decreased slightly from 1.2 to 1.0% and that of $^{38}ClO_3^-$ from 0.8 to 0.5%. The amount of $^{38}ClO^-$ present therefore could not have exceeded 0.5%, and consequently the "inverse annealing" in irradiated $KClO_2$ caused by heat must have resulted largely from the decomposition of ClO_2^-. No $^{38}ClO_4^-$ was found in the irradiated $KClO_2$.

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(30) A. E. Harvey, C. J. Wassink, T. A. Rodgers, and K. H. Stern, *Ann. N. Y. Acad. Sci.*, 79, 971 (1960).