Table II. Calculated Electronic Energies[a] for the Three Stationary Points of CrF_6 and Relative Energies[b] with Respect to the D_{3h} Isomer

geometry	O_h				D_{2d}		D_{3h}	
basis	A		B		A		A	B
SCF	−1639.555 58	+10.9	−1639.540 61	+12.0	−1639.555 60	+10.8	−1639.559 73	−1639.545 18
MP2	−1640.950 87	−67.9	−1640.795 38	−71.0	−1640.950 65	−67.3	−1640.925 02	−1640.768 36
MP3	−1640.511 84	+88.5	−1640.399 38	+84.8	−1640.512 76	+86.1	−1640.545 54	−1640.431 69
MP4DQ			−1640.659 64	−1.1				−1640.659 23
CCD			−1640.556 05	+19.5				−1640.563 47

[a] In atomic units (hartrees). [b] In units of kJ mol^{-1}.

species, it also has an imaginary frequency (e, $51i$ cm^{-1}). When all three t_{2u} components are considered, a D_{3h} structure is obtained (Figure 1b), which is 10.9 kJ mol^{-1} below the octahedral form *and* a true minimum. The Cr–F distance is 0.018 Å longer in the prism than in the octahedron, while the three F atoms on one prismatic face are closer together than in an octahedron. Structural data for these stationary points and calculated vibrational wavenumbers are presented in Table I, with energies in Table II. If it is remembered that vibrational frequencies calculated at the SCF level are generally overestimated by up to 10%,[15] the values predicted for the D_{3h} structure are not inconsistent with the single Cr–F stretching band reported[2] as the IR spectrum of matrix-isolated CrF_6 at 763 cm^{-1}. While Ogden and co-workers[2] naturally assigned this as the t_{1u} mode of an octahedral system, our calculated wavenumbers for the a_2'' and e' stretching modes for the prismatic structure of 818.2 and 817.4 cm^{-1} differ by only 0.8 cm^{-1}. (Note, however, that Jacob and Willner assert[3] that the band at 763 cm^{-1} is in fact due to CrF_5.)

Geometry optimization at correlated levels was not feasible. All correlated energies were obtained at the SCF geometries optimized with basis A. Corelike orbitals and their corresponding vituals were "frozen". While perturbation theory offers the simplest approach to calculating correlation energies, the MP series unfortunately oscillates pathologically; the MP2 energy is much larger than expected, at −1.3953 au for the octahedral isomer with basis A, and the change from MP2 to MP3 is +0.4391 au! We are unaware of any comparable system for which E3 is so large; the DZ(P)/MP2 energy for SF_6 is −0.8225 au, and E3 is just +0.0335 au. A single-reference description of CrF_6 is therefore poor, and perturbation-based correlated energies are unreliable. The most sophisticated correlated method available was CCD, but as the TZ basis A (125 functions) at this level was computationally too demanding, we adopted a DZ contraction (B, 96 functions) of the same primitives. CCD calculations converged slowly, consuming the equivalent of over 1 CPU-*month* on a Vax 11/780. The CCD margin of stability for the prismatic structure of CrF_6 over the octahedral is 19.5 kJ mol^{-1}, almost double the SCF value. These results strongly suggest that CrF_6 is prismatic, but they are probably not definitive, in view of the oscillations in the MP*n* energies. Kang, Albright, and Eisenstein have reported[4] that CrF_6 is octahedral at the MP2 level; however, their basis was much smaller than ours, and as we have shown that the MP2 method grossly overestimates the correlation energy, we believe their result is unreliable. CrF_6 certainly merits further theoretical and experimental attention.

Why is CrF_6 nonoctahedral, and why is it different from SF_6 or MoF_6? The pseudo-Jahn–Teller approach[16] is helpful; it predicts that if the HOMO–LUMO gap is small enough, distortions away from a symmetrical reference structure may be spontaneous if their symmetry species is contained in the direct product of the HOMO and LUMO representations. For octahedral CrF_6 and MoF_6, the HOMO has t_{1u} symmetry, while the LUMO is t_{2g}; the candidates for pseudo-Jahn–Teller distortions are therefore a_{2u}, e_u, t_{1u}, and t_{2u} species. These distortions are more likely to be associated with bending vibrations than stretching motions, due to the lower energy of the former. Both t_{1u} and t_{2u} bending vibrations are present for octahedral MX_6, but since the t_{2u} mode is invariably at lower frequency than the t_{1u},[17] a t_{2u} distortion may be anticipated for CrF_6. This is exactly the type of distortion predicted by our quantitative calculations. As the HOMO-LUMO gap is smaller for CrF_6 (0.465 au from our SCF results) than for MoF_6 (0.524 au), the pseudo-Jahn–Teller approach[16] predicts a greater tendency to distortion for CrF_6 than for MoF_6. The smaller HOMO–LUMO gap for CrF_6 than MoF_6 is caused both by the strongly oxidizing nature of Cr(VI), which lowers the Cr d orbitals (the t_{2g} LUMO), and by the F··F antibonding interactions, which destabilize the Cr–F nonbonding t_{1u} HOMO (these repulsions increase as the metal–F bond length decreases). For SF_6, with a t_{1g} HOMO, an a_{1g} LUMO, and a fairly large gap between them of 0.813 au, there is no symmetry-allowed pseudo-Jahn–Teller distortion, as there are no t_{1g} vibrations for octahedral MX_6. SF_6 is therefore much more rigidly octahedral than MoF_6; satisfyingly, the t_{2u} bending force constants F_{66} are 1.695[18] and 0.26[19] mdy Å rad^{-2}, respectively, showing the order of rigidity to be $SF_6 > MoF_6 > CrF_6$.

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Steady-State Voltammetry with Microelectrodes: Determination of Heterogeneous Charge-Transfer Rate Constants for Metalloporphyrin Complexes

The kinetics of heterogeneous electron transfer from an electrode to metalloporphyrin complexes in solution has been the subject of a number of publications in this journal and others.[1–6] Attempts have been made to correlate the corresponding standard heterogeneous charge-transfer rate constant, k_s, with the metal

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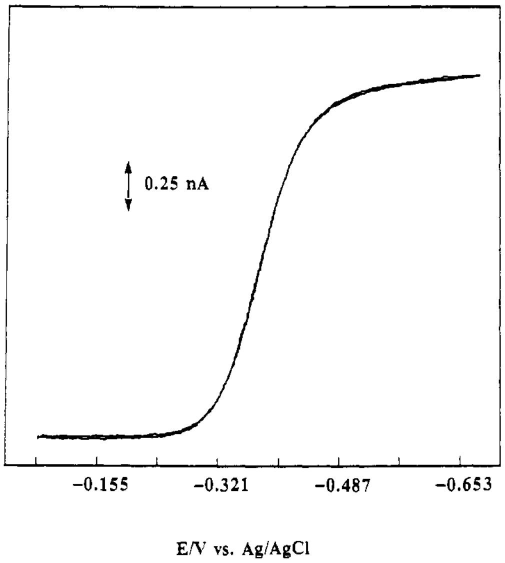

Figure 1. Cyclic voltammogram of 0.7 mM Fe(TPP)(*N*-MeIm)$_2^+$ in CH_2Cl_2 with 1.0 M *N*-MeIm and 0.1 M Bu_4NClO_4 at 25 °C. The working electrode was a 2-μm-diameter platinum disk, and the scan rate was 20 mV/s.

spin state, metal–ligand structural changes accompaning electron transfer, the site of electron transfer, and rates of homogeneous redox reactions. In these studies cyclic voltammetry with conventional electrodes was used to calculate the rate constant (k_s) from the scan rate dependence of the cathodic and anodic peak separation, ΔE_p, according to the prescription of Nicholson.[7] In organic solvents, especially relatively nonpolar ones such as dichloromethane, high resistance produces ohmic polarization that can lead to distortions in the voltammograms due to *iR* loss. While the effects of *iR* drop can be lessened by a variety of methods, e.g., use of a Luggin capillary, use of positive feedback compensation with potentiostatic control, and extrapolation to zero concentration of electroactive material (hence zero current), the total elimination of *iR* effects is not a simple matter. Unfortunately, the effect of uncompensated *iR* loss is difficult to distinguish from that expected for slow charge transfer. The purpose of this communication is to show that many previously reported charge-transfer rate constants for metalloporphyrins are incompatible with our results obtained with microelectrodes under conditions that are known to be free of distortions due to ohmic polarization.

It is now well established that voltammetry with microelectrodes (diameter < 100 μm), in comparison to conventional electrodes (diameter ≥ 1 mm), is much less influenced by solution resistance.[8,9] For example, recent work with microelectrodes has shown[10,11] that k_s for ferrocene oxidation at platinum and gold in various organic solvents is more than 1 order of magnitude larger than that calculated from data obtained with conventional electrodes; this illustrates the difficulty of completely eliminating distortions due to ohmic polarization with electrodes of traditional size[11] and argues strongly in favor of the use of microelectrodes for kinetic studies.

Cyclic voltammetry with microelectrodes at fast sweep rates may be used to measure relatively rapid charge-transfer rates, although corrections for charging current and *iR* distortions are normally required.[10,12] An alternative methodology utilizes the steady-state current response that obtains at low sweep rates (e.g., 20 mV/s) with the smaller microelectrodes (diameter ≤10 μm).[8,9,13] The steady-state response is due to convergent diffusion predominating over planar diffusion under these conditions and produces a cyclic voltammogram (CV) typified by Figure 1. The steady-state condition is especially attractive because it minimizes *iR* distortion to the point of being indetectable in most cases[14] and virtually eliminates interfering capacitive charging current.

Using steady-state voltammetry with platinum inlaid disk microelectrodes of diameter 25, 10, 5, 2, and 1 μm, fabricated as previously described,[15] we have determined the standard heterogeneous charge-transfer rate constants for a series of metalloporphyrins as well as ferricyanide reduction. Each compound studied was referenced to ferrocene, which gave a Nernstian (vide infra) steady-state CV at all electrodes, including the smallest, thus proving that *iR* distortions were inconsequential.

When the charge transfer is fast compared to mass transport (diffusion) processes, the CV is electrochemically reversible or Nernstian. Experimentally this is seen as $E_{1/2}$ and ($E_{1/4} - E_{3/4}$) values that do not depend on the electrode size. If the charge-transfer rate is comparable to the rate of mass transport to the electrode, the system is electrochemically quasi-reversible. Charge transfer much slower than mass transport defines an electrochemically irreversible system. For a reduction process, these effects are seen as a negative shift in $E_{1/2}$ and an increase in ($E_{1/4} - E_{3/4}$) from the reversible value of 56.5 mV at 25 °C to, in the irreversible limit, a value of $60.2/\alpha$, where α is the transfer coefficient. As the electrode size is decreased, the mass transport rate increases, and this means that the smaller the electrode, the more likely that the steady-state CV will show effects due to charge-transfer kinetics. From a practical viewpoint,[16] the CV will appear reversible if k_s is greater than ca. $100D/d$, where D is the diffusion coefficient and d is the electrode diameter. A k_s less than ca. $D/5d$ produces an irreversible wave; quasi-reversibility results when k_s is between these two values. Thus the effective "time scale" depends on the electrode size. Microelectrodes having $d > 1$ μm are fairly easily fabricated. In a recent report,[17] microelectrodes with diameters in the 20-Å range were described; steady-state voltammograms with electrodes of this size were shown to be sensitive to k_s values in excess of 100 cm/s, which is an extremely large rate constant.

Figure 1 shows a steady-state CV for the one-electron reduction of Fe(TPP)(*N*-MeIm)$_2^+$ in CH_2Cl_2 at a 2-μm platinum electrode. (TPP is the dianion of tetraphenylporphyrin; *N*-MeIm is *N*-methylimidazole.) On the basis of a Nicholson analysis of conventional CV's obtained with a 1-mm-diameter platinum electrode, it was reported[4] that $k_s = 0.040$ cm/s for this system. A number of procedures have been proposed concerning the analysis of steady-state CV's for effects of electrode kinetics.[16,19-21] The values of $E_{1/2}$ and ($E_{1/4} - E_{3/4}$) in the steady-state CV's of Fe(TPP)(*N*-MeIm)$_2^+$ showed that the reduction is close to being electrochemically reversible; in such a case it has been shown[16,19]

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Table I. Charge-Transfer Kinetic Parameters Determined by Steady-State Voltammetry[a]

complex	solvent	solution composn	$E°/V$	k_s/cm s^{-1}	α	reported[b] k_s/cm s^{-1}
$Fe(TPP)(N\text{-}MeIm)_2^+$	CH_2Cl_2	0.7 mM Fe(TPP)Cl, 1 M N-MeIm, 0.1 M Bu_4NClO_4	−0.40	0.35	0.58	0.040[c]
$Fe(OEP)(N\text{-}MeIm)_2^+$	CH_2Cl_2	0.8 mM Fe(OEP)Cl, 1 M N-MeIm, 0.1 M Bu_4NClO_4	−0.48	0.4	0.58	0.040[c]
$Fe(TPP)(HIm)_2^+$	CH_2Cl_2	0.5 mM Fe(TPP)Cl, 1 M HIm, 0.1 M Bu_4NClO_4	−0.39	0.5[d]		0.025[e]
$Fe(TPP)py_2^+$	CH_2Cl_2	0.5 mM $Fe(TPP)ClO_4$, 1 M py, 0.1 M Bu_4NClO_4	−0.03	0.6[d]		0.020[f,i]
$Mn(p\text{-}ClTPP)(DMSO)_2^+$	DMSO	2.0 mM Mn(p-ClTPP)Cl, 0.1 M Bu_4NClO_4	−0.26	0.006	0.60	0.0010[g,i]
Zn(TPP)	DMSO	2.0 mM Zn(TPP), 0.1 M Bu_4NClO_4	−1.35	>1		0.04[h]
$Fe(CN)_6^{3-}$	MeOH	0.5 mM $[Et_4N]_3Fe(CN)_6$, 0.1 M Et_4NClO_4	−0.25	0.02	0.65	0.02[i]
$Fe(CN)_6^{3-}$	H_2O	0.5 mM $K_3Fe(CN)_6$, 1 M KCl, 0.05 M NaCN	0.22[j]	0.05	0.42	0.04[i]

[a] At 25 °C; platinum microdisks of diameter 1–25 μm used; sweep rate 20 mV/s; reference electrode Ag/AgCl in solvent used; $E°$ values (except in water) are relative to Fc^+/Fc couple at +0.40 V. [b] Determined by cyclic voltammetry with conventional platinum electrodes (Nicholson method). [c] Reference 4. [d] Estimated error is ±50%. [e] Reference 6. [f] Reference 5. [g] Reference 2. [h] Reference 1. [i] This work. [j] Relative to Ag/AgCl.

that k_s and α may be obtained from plots of $E_{1/2}$ and $(E_{1/4} - E_{3/4})$ versus $1/d$. This treatment gave $k_s = 0.35$ cm/s and $\alpha = 0.58$. A more general method of analysis involves curve fitting the data to eq 1, which is an empirical relationship for a reduction at an

$$i_d/i = \theta + \pi(2\kappa\theta + 3\pi)/\kappa(4\kappa\theta + 3\pi^2) \qquad (1)$$

$$\theta = 1 + (D_O/D_R)\exp[nF(E - E°)/RT] \qquad (2)$$

$$\kappa = (\pi k_s d/8D_O)\exp[-\alpha nF(E - E°)/RT] \qquad (3)$$

inlaid disk that reproduces exact numerical solutions to a high degree of accuracy and applies whatever the degree of electrochemical reversibility.[16,22] In eq 1, i_d is the diffusion-limited current, $E°$ is the standard reduction potential, and D_O and D_R are the diffusion coefficients of the oxidized and reduced species, respectively, which were assumed to be equal. Each steady-state CV was collected with a digital oscilloscope and transferred to a computer for fitting to eq 1 with Asystant Plus software.[23] The CV's were defined with at least 100 data points, which were used in the nonlinear least-squares routine. Although in principle eq 1 can be fitted to yield values of $E°$, k_s, and α, in practice useful results are obtained only if $E°$ is known. In this work, $E°$ was obtained from conventional CV's, from extrapolation of the steady-state $E_{1/2}$ to a zero value of $1/d$ for nearly reversible systems,[19] or from potentiometric measurements. Fitting the CV's for $Fe(TPP)(N\text{-}MeIm)_2^+$ (e.g., Figure 1) to eq 1 gave $k_s = 0.3$ cm/s and $\alpha = 0.5$ ($R^2 = 0.999$). The k_s and α parameters in eq 1 are sufficiently cross-correlated that excellent fits were also obtained when α was fixed at any value in the range 0.4–0.6. For this reason, the data were analyzed by an additional method, as described below.

It has been shown[18,20-22] that the steady-state response at a microdisk electrode is very nearly the same as that at an equivalent hemispherical electrode. We use the definition[22] that a disk of diameter d is equivalent to a hemisphere of diameter $2d/\pi$ because this implies identical limiting diffusion currents for both types of geometry, namely, $i_d = 2nFCDd$. For the equivalent hemisphere, the current–potential relationship is given[22,24] by eq 4,

$$i_d/i = \theta + \pi^2/8\kappa = 1 + \exp[nF(E - E°)/RT] + (\pi D_O/k_f)(1/d) \qquad (4)$$

$$k_f = k_s\exp[-\alpha nF(E - E°)/RT] \qquad (5)$$

$$\ln k_f = \ln k_s + \alpha nFE°/RT - \alpha nFE/RT \qquad (6)$$

where k_f is the charge-transfer rate constant at potential E, as defined in eqs 5 and 6. Equation 4 was applied to the steady-state CV's for $Fe(TPP)(N\text{-}MeIm)_2^+$ by plotting i_d/i versus $1/d$ at a fixed potential E for microelectrodes in the range 25–1 μm. This was repeated at six different potentials that spanned most of the voltammetric wave. The slope of each plot gave k_f at the specified potential (D_O was calculated from the magnitude of i_d). A final plot of ln k_f versus E yielded k_s and α from the intercept and slope according to eq 6. The results are $k_s = 0.39$ cm/s and $\alpha = 0.58$. Equation 4 is similar to expressions previously reported[18,20,21] that utilize a different definition of disk-hemisphere equivalence; use of these left α unchanged but lowered k_s by 20% to 0.31 cm/s. If CV's are available for only a single size of microelectrode, eq 4 can be recast as eq 7 and the relevant kinetic parameters extracted by plotting E versus ln {}. In general, we found that data treatment according to eq 4 gave highly linear plots for the various compounds studied. Furthermore, k_s and α were found to be only mildly sensitive to substantial errors (5–10%) in locating the limiting current plateau (i_d).

$$E = E° - (RT/\alpha nF)\ln(\pi D_O/k_s d) + (RT/\alpha nF)\ln\{(i_d/i) - 1 - \exp[nF(E - E°)/RT]\} \qquad (7)$$

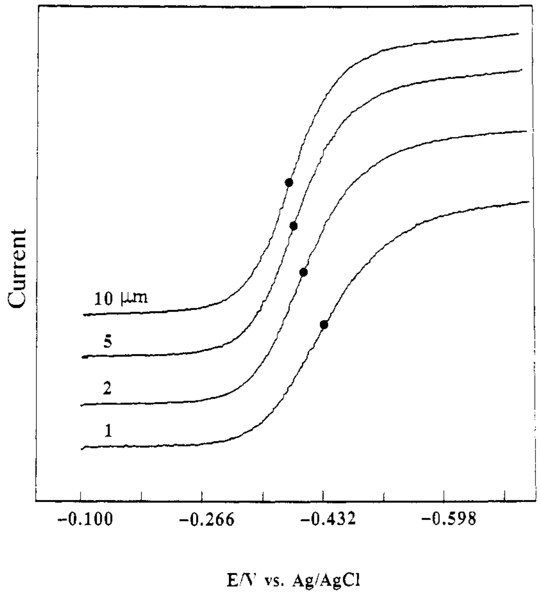

Figure 2. Steady-state voltammograms of 2.0 mM $Mn(p\text{-}ClTPP)(DMSO)_2^+$ in DMSO with 0.1 M Bu_4NClO_4 at 25 °C. The working electrodes were platinum disks of diameter 10, 5, 2, and 1 μm, and the scan rate was 20 mV/s. The current scale is normalized for each electrode. The solid dot marks the position of $E_{1/2}$.

Our conclusion is that k_s for the reduction of $Fe(TPP)(N\text{-}MeIm)_2^+$ in CH_2Cl_2/Bu_4NClO_4 is 0.35 ± 0.05 cm/s. This is about 10 times the previously reported[4] value, determined by conventional (transient) cyclic voltammetry. As discussed above, we ascribe this discrepancy to the difficulty of completely eliminating *iR* and charging current distortions in transient voltammetric measurements with conventional electrodes, especially in highly resistive solvents such as CH_2Cl_2. We have examined a number of previously reported metalloporphyrin systems using steady-state voltammetry at microelectrodes. With use of the analysis procedures described above, the results in Table I were obtained. Multiple measurements with each electrode size suggest that reasonable error limits are ±10% for α and ±20% for k_s, except

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as noted. The last column in Table I lists reported k_s values for metalloporphyrins as determined by cyclic voltammetry with conventional platinum electrodes (Nicholson method). In several cases we also used the Nicholson method, after attempting to correct ΔE_p for iR distortion by extrapolation to zero concentration and/or by substracting the iR drop shown by ferrocene (assumed to be reversible) at equivalent currents. Nevertheless, for the metalloporphyrins, the k_s obtained from steady-state experiments is significantly larger in each case. This is true for electron transfer ranging from quite slow for the metal-centered reduction of Mn(p-ClTPP)(DMSO)$_2^+$ to very rapid (reversible) for the ring-centered reduction of Zn(TPP). Figure 2 shows a series of steady-state voltammograms for the former complex; the slow electron transfer in this case is responsible for the negative shift of $E_{1/2}$ as the electrode size is decreased.

Table I also contains some results for the reduction of ferricyanide in methanol and water. After small iR corrections based on ferrocene were applied, the k_s in methanol obtained with a 1.6-mm platinum electrode matched from that found with microelectrodes under steady-state conditions. Likewise, the two procedures gave similar results in water/KCl. (The NaCN was present to prevent electrode fouling.[25]) The conclusion is that steady-state and transient methods indeed give the same results when the medium is sufficiently polar so that resistance effects are insignificant. It may be noted that the oxidation of potassium ferrocyanide in water has been examined by others with microelectrodes. At a 12-μm-diameter carbon fiber disk electrode (0.5 M KNO_3) a k_s of 0.02 cm/s was found[21] under steady-state conditions. At a 15-μm-diameter platinum microdisk (1.0 M HCl) the steady-state voltammogram suggests[26] a k_s of 0.07 cm/s; however, these authors inexplicably found the voltammogram at a much smaller platinum disk to have the same shape and concluded that the redox couple is reversible. At a 10-μm carbon fiber microdisk (pH = 1, $CF_3COOH/CF_3COO^-Na^+$ buffer) conventional CV's obtained at 500 V/s gave k_s = 0.06 cm/s by the Nicholson method, while at the same electrode under steady-state conditions the ferrocyanide oxidation was reported[27] to be reversible; this is inconsistent because a k_s of 0.06 cm/s predicts a steady-state voltammogram that deviates significantly from a reversible shape; e.g., the value of $(E_{3/4} - E_{1/4})$ should be 68 mV.

In summary, we found that heterogeneous charge-transfer rate constants determined by cyclic voltammetry with conventional electrodes are subject to large errors if the solutions used are highly resistive. Furthermore, the discrepancy between the apparent and the real k_s becomes greater as the electron transfer becomes more reversible. Elimination or correction for iR and charging current distortions is not simple. The use of microelectrodes under steady-state conditions eliminates most of the distortions and thus provides a convenient alternative procedure for studying the kinetics of charge transfer. It should be noted that steady-state voltammetry with microelectrodes can also be applied to the study of various types of *homogeneous* reactions coupled to the redox process.[28-30] Thus, microelectrodes permit both heterogeneous and homogeneous reactions to be examined without the distortions that plague experiments with conventional electrodes.

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A New Synthetic Route to the Preparation of a Series of Strong Photoreducing Agents: *fac* Tris-Ortho-Metalated Complexes of Iridium(III) with Substituted 2-Phenylpyridines

Current interest in the photophysics and photochemistry of ortho-metalated complexes of d^6 and d^8 metal ions such as Pt(II),[1-14] Ir(III),[13-23] Ru(II),[14,24,25] Pd(II)[10-14,26-30] and Rh-

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