the same strong faceting is yet again observed (Fig. 4F) (movie S1). This behavior was found to be ubiquitous, with all particles in He showing stronger faceting, and those in Ar exhibiting a more rounded shape.

We also investigated relatively larger catalyst sizes to more clearly observe the evolution of catalyst shapes. Figure 4G indicates that the equilibrium shape of the catalyst in the 500°C and 500 mtorr of He/H2O environment has {111} facets with very sharp edges, which is exactly the same observation as in Fig. 4D. Figure 4, H and I, (movie S2) tracks the gradual defaceting of the hill-and-valley structure with increasing time at the same temperature after the removal of He/H₂O and the addition of Ar/H₂O. All of the observations reflected in Fig. 4 are consistent: Catalysts in the He/H2O environment are strongly faceted. Additionally, the fact that the particles are more faceted in H₂/H₂O and He/H2O ambients is consistent with the observation of a reduced ripening rate.

Broadly, the adsorbent-induced variation of the surface free energy $\Delta \gamma$ of the facets with Miller indices (h, k, l) on the particle can be expressed by

$$\Delta \gamma_{h,k,l} = \Delta \gamma_{h,k,l}(P, T, C_{S}, \theta_{o}, k_{d}, S) \qquad (1$$

where P is the partial pressure of the adsorbate, Tis the temperature, $C_{\rm S}$ is the surface concentration of the particle surface atoms, θ_o is the saturation coverage of the adsorbate, $k_{\rm d}$ is the desorption rate constant, and S is the sticking probability of the adsorbate (21, 22). Our TEM data suggest that the surface energy anisotropy of specific facets of Fe is affected differently by the He/H2O and Ar/H2O ambients, resulting in the observed dynamic alterations in the particle shape. It is unlikely that the inert gas itself causes a difference in surface free energy via adsorption at high temperatures. Therefore, the entirety of our data set indicates that it is most probable that H₂O adsorption is responsible for the induced surface reconstruction (23). The adsorption pathway can be either dissociative (with formation of adsorbed hydroxyl, atomic oxygen, and atomic hydrogen species on the surface) or molecular (24). However, analysis of the catalyst structure (through the use of diffractograms produced by fast Fourier transforms of the images, shown as an inset to Fig. 4G, indicating that the particles are γ -Fe) and observation of reversible shape changes (Fig. 4, D to F) suggest that there is no strong oxygen binding, which could have an impact on tube growth (25, 26). The TEM measurements were performed under conditions of dynamic adsorption/desorption equilibrium with both H₂O and either He or Ar gas present. Both the observation of an adsorbentinduced reversible shape reconstruction and severe particle ripening under the Ar/H2O environment (fig. S6) are consistent with the adatom's coverage of the Fe particles being greater in the He versus the Ar ambient $[\theta_{(\text{He}+\text{H2O})} > \theta_{(\text{Ar}+\text{H2O})}]$. This would also be correlated to the resulting,

relatively low density of grown tubes under Ar-supported ambient (fig. S1). Thus, it appears that the addition of H₂O not only assists the super growth of nanotubes by etching the amorphous carbon (27) and controls the particle diameter by retarding the effect of Ostwald ripening (28), but also alters the shape of the particle. Remarkably, Yamada et al. (29) observed the alteration of carbon coated Fe catalysts into flatter particles upon the removal of the carbon coating by water treatment, under standard water-assisted nanotube growth conditions. There are other adsorbates (such as CO and O_2) that, in combination with the carbon source, may be even more effective at altering the catalyst size and morphology. Our results indicate that, with further optimization, direct control over nanotube structure during growth may well be feasible (30, 31).

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Supporting Online Material

www.sciencemag.org/cgi/content/full/326/5949/116/DC1 Materials and Methods Figs. S1 to S6 Table S1 References Movies S1 and S2

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Chiral Organic Ion Pair Catalysts Assembled Through a Hydrogen-Bonding Network

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Research to develop structurally discrete, chiral supramolecular catalysts for asymmetric organic transformations has met with limited success. Here, we report that a chiral tetraaminophosphonium cation, two phenols, and a phenoxide anion appear to self-assemble into a catalytically active supramolecular architecture through intermolecular hydrogen bonding. The structure of the resulting molecular assembly was determined in the solid state by means of x-ray diffraction analysis. Furthermore, in solution the complex promotes a highly stereoselective conjugate addition of acyl anion equivalents to α , β -unsaturated ester surrogates with a broad substrate scope. All structural components of the catalyst cooperatively participate in the stereocontrolling event.

Ature harnesses weak interactions, particularly hydrogen bonds, to construct biologically active supramolecular architectures, as demonstrated by the three-dimensional structures of enzymes and nucleic acids. Inspired by these biological systems, research for the development and application of supramolecular catalysts assembled through noncovalent interactions has attracted interest in the fields of both selective chemical synthesis and molec-

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Fig. 1. (A) Structures of chiral tetraaminophosphonium cations. (B) Oak Ridge thermal ellipsoid plot diagram of 1a · (OPh)₃H₂. All calculated hydrogens were omitted for clarity. (C) Plausible modes of assembly in catalyst and enolate.

of discrete molecular associations remains a great challenge (1–5). Described here are systems in which chiral and achiral small molecules spontaneously assemble through a well-defined array of intermolecular hydrogen bonds to produce structured chiral organic ion pairs. The distinctive feature of the supramolecular ion pair assembly as a chiral molecular catalyst is that its stereocontrolling ability can be fine-tuned by structural modification of both chiral and achiral components. We developed a catalyst for the highly enantioselective conjugate addition of acyl anion equivalents to α , β -unsaturated ester surrogates.

We initially prepared chiral tetraaminophosphonium phenoxides as part of our broader exploration of chiral organic ion pairs for cooperative asymmetric catalysis (6). The requisite cation framework 1a (Fig. 1A) was readily synthesized from the parent a-amino acid, L-valine, as its chloride salt (7). Then, the anion was exchanged with hydroxide, and subsequent neutralization with phenol (8) yielded 1a (OPh)₃H₂. The solidstate structure of 1a (OPh)₃H₂ was unambiguously determined by means of single-crystal x-ray diffraction analysis (Fig. 1B). Surprisingly, the analysis revealed a molecular assembly in which an aminophosphonium cation, two phenols, and a phenoxide anion were aligned through a 10membered cyclic network of intermolecular hydrogen-bonding interactions. The hydrogenbonding donor capability of the phenols seems to be enhanced by an additional hydrogen bond from the N-H protons of the phosphonium cation, thus facilitating the construction of an antidromic circular network (9-11). Another salient feature of the assembly was that the stereochemical information in the chiral cation moiety was effectively relayed by the two phenol molecules, extending

Table 1. Effect of each component of the catalyst assembly. Unless otherwise noted, the reactions were performed with 0.22 mmol of **2** and 0.2 mmol of **3a** in the presence of catalyst (1 mol %) in 2.0 mL of toluene at -40°C under argon atmosphere. The catalyst concentrations are indicated. The isolated yields are reported. All diastereomeric ratios (dr) and ee were determined by means of ¹H nuclear magnetic resonance (NMR) (500 MHz) analysis of crude aliquots and chiral stationary phase high-performance liquid chromatography (HPLC), respectively. The relative stereochemistry was not determined.



Entry	Catalyst	Conc (mM)	Time (h)	Yield (%)	ee (%)
1	$1a \cdot (PhO)_3H_2$	1	6	99	60
2	1a'	1	2	99	34
3	1a' + 3PhOH	1	10	98	62
4	1a·2' + 3PhOH	1	16	87	61
5	$1a \cdot (4 - Me - C_6 H_4 O)_3 H_2$	1	4	96	58
6	$1a \cdot (4 - Cl - C_6 H_4 O)_3 H_2$	1	10	97	75
7	$1a \cdot (2 - Cl - C_6 H_4 O)_3 H_2$	1	12	94	63
8	$1a \cdot (3 - Cl - C_6 H_4 O)_3 H_2$	1	6	93	70
9	$1a \cdot (3,5 - Cl_2 - C_6 H_3 O)_3 H_2$	1	16	92	80
10*	$1a \cdot (3,5 - Cl_2 - C_6 H_3 O)_3 H_2$	2	24	99	85
11†	$1a \cdot (3,5 - Cl_2 - C_6 H_3 O)_3 H_2$	5	18	98	89
12‡	$1a \cdot (3,5 - Cl_2 - C_6 H_3 O)_3 H_2$	10	20	94	89
13§	1a·(3,5-Cl2-C6H3O)3H2	10	4	99	87
14§	$1b(3,5-Cl_2-C_6H_3O)_3H_2$	10	4	95	95
a mal % of catalyst was used +Eive mal % of		catalyst was used	+Ten mol % of catalyst was used		60.2 r

the chiral environment around the remotely located phenoxide anion.

On the basis of these serendipitous observations, we explored the use of $1 \cdot (OAr)_3 H_2$ as a chiral molecular catalyst for synthetically valuable stereoselective transformations. For this pur-

pose, we chose 2-unsubstituted oxazol-5(4*H*)-one, namely azlactone, **2** (Fig. 1C and Table 1) as a pro-C1-nucleophile (*12*) with the expectation that the enolate **2'** generated through deprotonation by $\mathbf{1} \cdot (OAr)_3 H_2$ would behave as a suitable phenoxide anion equivalent; as such, it would **Table 2.** Scope of α , β -unsaturated acylbenzotriazole **3.** The reactions were performed with 0.22 mmol of **2** and 0.2 mmol of **3** under the influence of **1b** · (3,5-Cl₂-C₆H₃O)₃H₂ (1 mol %) in 0.2 mL of toluene at -40°C under argon atmosphere. The isolated yields are reported. All dr and ee were determined by means of ¹H NMR (500 MHz) analysis of crude aliquots and chiral stationary phase HPLC, respectively.



Entry	R (3)	Time (h)	Yield (%)	ee (%)	Prod
1	$4-MeO-C_6H_4$ (3b)	24	98	97	4b
2	$4-Br-C_{6}H_{4}(3c)$	21	98	98	4 c
3	$2-Me-C_6H_4$ (3d)	8	90	93	4d
4	$3-Br-C_6H_4$ (3e)	4	96	95	4 e
5	1-Naph (3f)	12	91	95	4f
6	2-Furyl (3g)	22	91	96	4g
7	Me (3h)	2	97	96	4h*
8	Me(CH ₂) ₄ (3i)	1	96	95	4i
9	Ph(CH ₂) ₂ (3j)	2	92	96	4j
10	Cyclohexyl (3k)	4	93	98	4 k

^{*}Absolute configuration of the product **4h** was determined, after conversion to the known compound **6** (Fig. 2), by comparison of the optical rotation with the literature value (7).

Fig. 2. Conversion of **4h** to optically active methylsuccinic acid **6**. DBU, **1**,8-diazabicyclo[5.4.0] undec-7-ene; Ac, acetyl; THF, tetrahydrofuran.

be captured into a similar hydrogen-bonding network without negatively affecting the preorganization [$1a\cdot(OPh)_2H_2$ ·**2'**] (Fig. 1C). If this held true, the structures of not only the chiral aminophosphonium cations but also the achiral phenols would affect the stereo-determining step of the addition reaction of the enolate **2'**. To verify this hypothetical synergistic effect of the structural components of the supramolecularly assembled ion-pair catalyst, we examined the conjugate addition of **2** to α,β -unsaturated acylbenzotriazole **3** (*13*), a reactive and readily derivatizable Michael acceptor, under the influence of $1\cdot(OAr)_3H_2$.

The initial attempt entailed stirring a mixture of **2**, **3a**, and $1a \cdot (OPh)_3H_2$ in toluene at $-40^{\circ}C$, giving rise to essentially diastereomerically pure adduct **4a** in a quantitative yield with 60% enantiomeric excess (ee) (Table 1, entry 1). In contrast, use of the independently prepared conjugate base of **1a** (triaminoiminophosphorane **1a'**) (Fig. 1C) (*14*) as a catalyst led to the formation of **4a** with 34% ee (entry 2). These results clearly indicate the importance of the phenolic component of $1a \cdot (OPh)_3H_2$ in enhancing enantioselectivity. Whereas the reaction with **1a'** proceeds through the generation of chiral aminophosphonium enolate $1a \cdot 2'$, the expected, highly organized $1a \cdot (OPh)_2 H_2 \cdot 2'$ complex could be involved in the $1a \cdot (OPh)_3 H_2$ -catalyzed system, and the two phenols may play a key role in creating an attractive chiral environment around the azlactone enolate 2'.

Treatment of iminophosphorane 1a' with phenol (3 equiv), followed by the sequential addition of 3a and 2, resulted in the formation of 4a in 98% yield with 62% ee after 10 hours of stirring (entry 3). The reactivity and selectivity were scarcely affected by the order of the addition of phenol and azlactone 2 (entry 4). These results suggest that the preorganization of the catalyst is not a prerequisite for the generation of $1a \cdot (OPh)_2 H_2 \cdot 2'$, which could be self-assembled from 1a', phenols, and 2 by way of either 1a·(OPh)₃H₂ or 1a·2'. These observations implied that the selectivity could be tunable through structural modification of the achiral phenolic component. Indeed, although the selectivity decreased when phenols of 1a (OPh)₃H₂ were replaced by 4-methylphenol, a series of chloro-substituted phenols, particularly 3,5-

dichlorophenol, induced substantial increases in enantioselectivity (entries 5 to 9) (table S1 and SOM text). Furthermore, we confirmed the effect of the catalyst concentration on the propensity for molecular association in solution. As we had assumed, both increased catalyst loading and decreased solvent volume improved enantioselectivity (entries 10 to 12 and 13), which also argues for the role of a requisite molecular assembly (fig. S1 and SOM text). Structural modification of the chiral cationic moiety by using L-isoleucine-derived 1b (see Fig. 1A) also appeared to be crucial for achieving the highest selectivity (entry 14). Consequently, all the structural components of the self-assembled catalyst cooperatively participate in realizing the rigorous stereocontrol.

With the optimal catalyst structure and reaction conditions in hand, we conducted further experiments to probe the scope of α , β -unsaturated acylbenzotriazole 3, and the representative results are summarized in Table 2. Generally, use of 1 mole percent (mol %) of $1b(3,5-Cl_2-C_6H_3O)_3H_2$ and 1.1 equivalents of 2 was sufficient for a smooth reaction, giving 4 in high yield with excellent enantioselectivity. With aryl-substituted 3, this method tolerated the incorporation of both electronwithdrawing and electron-donating substituents at an arbitrary position on the aromatic scaffold (entries 1 to 4). In addition, fused- and heteroaromatic β -substituents had no influence on the stereochemical outcome (entries 5 and 6). A range of primary and secondary alkyl groups were also nicely accommodated (entries 7 to 10).

The acylbenzotriazole and azlactone moieties of product **4** can be selectively converted to various useful functional groups, thus highlighting the synthetic potential of the present highly stereoselective conjugate addition protocol. For example, **4h** (96% ee) was successfully derivatized into optically active methylsuccinic acid (**6**) in four steps without loss of the enantiomeric excess (Fig. 2).

We believe these results encourage further research efforts to determine the minimal chiral or achiral structural bias necessary to induce spontaneous yet discrete associations between simple organic molecules through weak noncovalent interactions. The resultant catalytically active and selective structures may greatly expand the possibilities for designing functional supramolecular catalysts.

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Nitrous Oxide (N₂O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century

A. R. Ravishankara,* John S. Daniel, Robert W. Portmann

By comparing the ozone depletion potential—weighted anthropogenic emissions of N_2O with those of other ozone-depleting substances, we show that N_2O emission currently is the single most important ozone-depleting emission and is expected to remain the largest throughout the 21st century. N_2O is unregulated by the Montreal Protocol. Limiting future N_2O emissions would enhance the recovery of the ozone layer from its depleted state and would also reduce the anthropogenic forcing of the climate system, representing a win-win for both ozone and climate.

The depletion of the stratospheric ozone layer by human-made chemicals, referred to as ozone-depleting substances (ODSs), was one of the major environmental issues of the 20th century. The Montreal Protocol on Substances That Deplete the Ozone Layer (1), MP, emerged from the Vienna Convention for the Protection of the Ozone Layer (2). The MP has been highly successful in reducing the emissions, growth rates, and concentrations of chlorine- and brominecontaining halocarbons, the historically dominant ODSs (3), and has limited ozone depletion and initiated the recovery of the ozone layer.

The relative contributions of various ODSs to ozone layer depletion are often quantified by the ozone depletion potential (ODP) (4). An ODP relates the amount of stratospheric ozone destroyed by the release of a unit mass of a chemical at Earth's surface to the amount destroyed by the release of a unit mass of chlorofluorocarbon 11, CFC-11 (CFCl₃). ODPs are widely used for policy formulation because of their simplicity in quantifying the relative ozone-destroying capabilities of compounds.

Through the work of Crutzen (5) and Johnston (6), nitrogen oxides (NO_x = NO + NO₂) are also known to catalytically destroy ozone via

$$\begin{split} & \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \\ & \text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \\ & \text{net: } \text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \end{split}$$

Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80305, USA. The primary source of stratospheric NO_x is surface N₂O emissions [(7) and references therein]. N₂O has been thought of as primarily a natural atmospheric constituent, but the influence of its changes on long-term changes in ozone concentrations has also been examined (8–10).

Nitrous oxide shares many similarities with the CFCs, historically the dominant ODSs. The CFCs and N₂O are very stable in the troposphere, where they are emitted, and are transported to the stratosphere where they release active chemicals that destroy stratospheric ozone through chlorine- or nitrogen oxide–catalyzed processes. They both have substantial anthropogenic sources. Unlike CFCs, N₂O also has natural sources, akin to methyl bromide, which is another important ODS. Assigning an ODP for N₂O and separating out the natural and anthropogenic emissions are therefore no more conceptually difficult than they are for methyl bromide.

In spite of these similarities between N_2O and previously recognized ODSs and in spite of the recognition of the impact of N_2O on stratospheric ozone, N_2O has not been considered to be an ODS in the same sense as chlorine- and bromine-containing source gases. The signatories to the Vienna Convention (2) have agreed in Article 2 (General Obligations) to "Adopt appropriate legislative or administrative measures ... to control, limit, reduce or prevent human activities under their jurisdiction or control should it be found that these activities have or are likely to have adverse effects resulting from modification or likely modification of the ozone layer." Yet N_2O remains unregulated by the MP (1).

Here, we present the ODP of N₂O to be positive and nonzero and show that N₂O is an ozone-

Supporting Online Material

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depleting substance on the basis of the extent of ozone depletion it causes. Indeed, current anthropogenic ODP-weighted N₂O emissions are the largest of all the ODSs and are projected to remain the largest for the rest of the 21st century.

We have calculated the ODP of N2O by using the Garcia and Solomon two-dimensional (2D) model [(11) and references therein], which is similar to models used previously for such calculations (12, 13). The ODP of N₂O under current atmospheric conditions is computed to be 0.017. This value is comparable to the ODPs of many hydrochlorofluorocarbons (HCFCs) (3) such as HCFC-123 (0.02), -124 (0.022), -225ca (0.025), and -225cb (0.033) that are currently being phased out under the MP. We conclude that the value of the ODP of N2O is robust because (i) our similarly calculated ODPs for CFC-12 (1.03) and HCFC-22 (0.06) agree with the accepted values (3); (ii) ozone depletion by NO_r from N2O dominates the chemical control of ozone in the mid-stratosphere (13), a region well represented with 2D models; and (iii) ozone reductions by enhanced N2O have been reported in other studies (8, 10, 14), although no published study, to the best of our knowledge, has previously presented an ODP for N2O.

We examine here a few important factors that influence the ODP of N₂O. At mid-latitudes, chlorine-catalyzed ozone destruction contributes most to depletion in the lowest and upper stratospheres, that is, below and above the ozone maximum. Nitrogen oxides contribute most to ozone depletion just above where ozone concentrations are the largest. This leads to efficient ozone destruction from NO_x (13). The ODP of N₂O is lower than that of CFCs primarily because only ~10% of N₂O is converted to NO_x, whereas the CFCs potentially contribute all their chlorine.

There are important interconnections between the roles of nitrogen oxides with chlorine such that the N₂O ODP may be different from the calculated value in the past and future. It is well known that nitrogen oxides dampen the effect of chlorine-catalyzed ozone destruction via the formation of ClONO₂, which ties up some of the chlorine in a benign form. However, as shown by Kinnison *et al.* (9), other reactions, such as the conversion of ClO to Cl by NO, can offset the damping.

We quantify the dependence of the ODP of N_2O on atmospheric concentrations of chorine by calculating it for 1959 concentrations of strato-

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